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Stabilizing Double Perovskite for Effective Bifunctional Oxygen Electrocatalysis in Alkaline Conditions

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Supporting Information

ABSTRACT: Oxygen electrocatalysis is at the heart of the emerging energy conversion and storage devices including reversible fuel cells and metal-air batteries. However, replacing the noble-metal-based oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) catalysts with affordable and robust alternatives remains challenging to date. Herein, we report a cation-ordered double perovskite oxide, i.e., $\text{PrBa}_{0.85}\text{Ca}_{0.15}\text{MnFeO}_{5+\delta}$ with excellent stability and activity in both OER and ORR. The layered crystal structure provides ordered oxygen vacancy channels and a vast amount of surface oxygen defects, while the moderate amount of iron dopant keeps the B-site cations at high oxidation state with optimal e_g fillings. Importantly, the DFT calculations along with the advanced TEM analysis verify that the incorporation of Ca at the A-site stabilizes the perovskite structure under potential bias. Such a bifunctional catalyst shows comparable, if not better, activity relative to the state-of-the-art perovskite oxides (e.g., $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) while demonstrating remarkably enhanced robustness. This work presents a rational approach of designing efficient, robust, and cost-effective perovskite oxide for oxygen electrocatalysis and sheds light on the influences of the crystallographic structure on the catalytic property.

1. INTRODUCTION

The development of highly efficient energy conversion and storage devices plays a key role in dealing with the grand energy challenge today. Oxygen electrocatalysis, in both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), is at the heart of these emerging devices including reversible fuel cells and metal-air batteries.^{1–6} Despite the tremendous efforts from the catalysis community, finding low-cost and high-efficient ORR and OER catalysts remains a difficult task.^{7–10} In particular, the sluggish ORR kinetics in fuel cells make the cathode catalyst selection highly rest on the Pt-based materials. Meanwhile, the search for active, yet inexpensive, OER catalysts for water-splitting/energy storage applications is also an outstanding problem to date.

Indeed, noble metals and their alloys and oxides, such as Pt, Pt alloys, IrO_2 , and RuO_2 , are the state-of-the-art catalysts for oxygen catalysis.^{7–9,11–13} However, the high price and the element scarcity hinder their scalable applications. Recently, perovskite oxide (ABO_3) comes into view in a range of electrochemical devices as a high-performance, low-cost catalyst.^{1–3,5,6,10,14–17} In particular, the double perovskite oxide has shown excellent performance–cost balance and is recognized as an ideal substitute of precious metals in oxygen

electrocatalysis.^{16,18–21} Kahoul reported that the $\text{Sr}_{1.5}\text{La}_{0.5}\text{FeMoO}_6$ double perovskite exhibited the best electrocatalytic activity for both ORR and OER among the $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.25, 0.5$, and 1) series.²¹ The Shao-Horn's group found that the double perovskite $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Gd}$, and Ho) family was highly active and stable for OER in alkaline conditions.¹⁸ We also investigated a series of double perovskites, $\text{NdBa}_{0.75}\text{Ca}_{0.25}\text{Co}_x\text{Fe}_{2-x}\text{O}_{5+\delta}$ ($x = 2, 1.5, 1, 0.5$), as promising ORR catalysts.¹⁶ Nevertheless, a number of outstanding issues regarding the perovskite electrocatalysts need to be addressed more appropriately. For instance, perovskite-type catalysts can suffer from degradations in the long-term operation because of the gradual crystal-structure and surface-property change. It is driven dynamically by various parameters of the surrounding environments, e.g., temperature, pH value, oxygen partial pressure, stress state, and electrochemical potential.^{22–25} The dopant segregation at the surface and/or the interfaces (e.g., grain boundary and phase boundary) is one of the typical problems in ORR.^{24–27} In

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Figure 1. (a) A schematic of the synthesis process and the crystal-structure evolution of PBCMF-1 compound. (b) XRD patterns of cation-disordered D-PBCMF-1 and cation-ordered PBCMF-1. (c) Raman spectra imply the ideal layered perovskite structure of PBCMF-1 with $P4/nmm$ symmetry. (d) TGA test of PBCMF-1 in 10% H₂-90% N₂, showing that the structures of air-prepared PBCMF-1 could be tuned by treating in H₂. Atom-resolved HRTEM micrographs of (e) D-PBCMF-1 and (f) PBCMF-1; the green, purple, and yellow spheres in the insets represent Ba/Ca, Pr, and Mn/Fe atoms, respectively. Note that the atom arrangement of Pr and Ba/Ca is representative, showing the cation (dis)ordering.

addition, the surface amorphization, a process in which the surface layer loses its crystallinity, could also occur during the prolonged OER cycles.^{23,28,29} Both of these surface decomposition and reconstruction can severely impair the stability, conductivity, and activity of the catalyst.

Though it is generally agreed that the structural stability of the perovskite is strongly correlated with the stability of the B-site octahedral (BO₆),²² the partial substitution of the A-site cations by one with a different valence and radius could also effectively enhance both the stability and the activity.^{16,25} Herein, on the basis of the advanced microscopic analysis and the computational modeling, we optimize the crystal structure and the dopant composition of the candidate catalyst. The developed cation-ordered double perovskite oxide, i.e., PrBa_{0.85}Ca_{0.15}MnFeO_{5+δ}, exhibits excellent activity in both OER and ORR in alkaline conditions. More importantly, both the cation enrichment and the amorphization at the surface are prevented during the electrocatalytic reactions, rendering drastically improved stability. Comparing with the commonly used cobalt-containing perovskites, our catalyst not only exhibits analogously high performance but also shows good cost effectiveness (cobalt is more expensive than Mn and Fe). This work presents a rational approach in designing an efficient, robust, and cost-effective bifunctional perovskite-based electro-

catalyst for oxygen electrocatalysis and sheds light on the influences of the crystallographic structure on the catalytic activity.

2. RESULTS AND DISCUSSION

The cation-ordered double perovskite PBCMF-1 was obtained via a facile two-step synthesis method: initially, the cation-disordered (PrBa_{0.85}Ca_{0.15})_{0.5}(MnFe)_{0.5}O_{3-δ} (D-PBCMF-1) perovskite phase was obtained via the classical Pechini method after the 950 °C calcination; the as-prepared powder was then annealed in 5% H₂-95% N₂ at 600 °C to acquire the cation-ordered structure (see Figure 1a). In the controls, we also prepared PrBaMn₂O_{5+δ} (PBM), PrBaMn_{1.5}Fe_{0.5}O_{5+δ} (PBMF-0.5), PrBaMnFeO_{5+δ} (PBMF-1), PrBaMn_{0.5}Fe_{1.5}O_{5+δ} (PBMF-1.5), and PrBaFe₂O_{5+δ} (PBF) powders (summarized in Table S1). A detailed preparation protocol is shown in the Experimental Section (*vide infra*). Thanks for the phase transformation, the Mn(Fe)O₂ sublattice in the double perovskite is sandwiched by two rock-salt layers, PrO_x and Ba(Ca)O, forming long-range ordered oxygen vacancy sites at the PrO_x layers (see the schematic in Figure 1a). Such a defect structure will increase the oxygen diffusion rate in the bulk, which has already been recognized to be beneficial to facilitating diverse electrocatalytic reactions.^{3,16,30–32}

Figure 2. (a) LSV curves of $\text{PrBaMn}_x\text{Fe}_{2-x}\text{O}_{5+\delta}$ catalysts for ORR in O_2 -saturated KOH. (b) LSV curves of PBMF-1, PBCMF-1, D-PBCMF-1, and Pt/C catalysts for ORR in O_2 -saturated KOH. (c) LSV curves of PBCMF-1 at different rotating speeds, and the corresponding K-L plot is inserted. (d) LSV curves of PBMF-1, PBCMF-1, D-PBCMF-1, PBF, and BSCF catalysts for OER in Ar-saturated KOH. (e) Tafel plots of PBMF-1, PBCMF-1, and BSCF catalysts for OER in Ar-saturated KOH. (f) ORR and OER stability tests of the PBMF-1 and PBCMF-1 catalysts (the ORR stability test was performed at initial $E_{1/2}$ in O_2 -saturated KOH, while the OER stability test was performed in Ar-saturated KOH and at constant potentials to ensure an initial current density of 5 mA cm^{-2}). (g) Comparison of the ORR $E_{1/2}$ before and after the durability test ORR described in (f). (h) Comparison of the OER overpotentials before and after the OER durability test described in (f).

We then used multiple characterization techniques to verify the formation of the cation-ordered structure. In comparison with the X-ray diffraction (XRD) pattern of D-PBCMF-1, the one of PBCMF-1 in Figure 1b clearly shows a layered structure without disordered phases (see also the XRD patterns in Figure S1 for the related samples). A sequential Rietveld refinement revealed that the space group of D-PBCMF-1 changed from a $Pm\bar{3}m$ to a tetragonal symmetry ($P4/nmm$) after the H_2 annealing. The dimension along the c -axis in the unit cell doubled, reflecting the formation of a double perovskite structure (see the complete lattice parameters in Table S2).^{30,31} Raman spectra manifested that the layered perovskite PBCMF-1 with $P4/nmm$ symmetry exhibited an ordered structure, since no peak has been detected. Instead, the appearance of a broad vibration band at $\approx 675 \text{ cm}^{-1}$ for D-PBCMF-1 is attributed to the internal motion of oxygen within the $\text{Mn}(\text{Fe})\text{O}_6$ octahedra, which is strongly correlated to the Jahn–Teller distortion in D-PBCMF-1 crystal (Figure 1c). According to the previous works,^{30,31} the crystal reconstruction to double perovskite is typically accompanied by the rapid loss of nonstoichiometric oxygen. In the thermogravimetric analysis (TGA) in Figure 1d, we recorded a rapid mass loss of D-PBCMF-1 at ca. 400°C in the stream of diluted H_2 , which is an additional evidence indicating the phase transformation (additional results are shown in Figure S2). Similar observations were also reported during the phase transformation from $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ and $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$ to $\text{PrBaMn}_{2-x}\text{O}_{5+\delta}$ and $\text{PrBaMn}_{1.8}\text{Co}_{0.2}\text{O}_{5+\delta}$, respectively.^{30,31}

The crystal structure evolution was also observed using the atom-resolved high resolution transmission electron microscope (HRTEM) as shown in Figure 1e,f. The diffractogram obtained from the selected area electron diffraction affirmed the

$Pm\bar{3}m$ space group of D-PBCMF. After the crystal reconstruction, there were strong superlattice reflections at $\pm 1/2$ (001)* of the fast-Fourier transformed (FFT) pattern, which was ascribed to the formation of the tetragonal system with a doubled c -axis. A schematic atom arrangement of Pr and Ba/Ca is shown in the insets, representing the cation (dis)ordering of the oxide. Additionally, the d -spacings of the (001) plane for D-PBCMF-1 and PBCMF-1 were 3.95 and 7.86 Å, respectively. These values were roughly identical with those obtained through the XRD refinement (Table S2) and confirmed the lattice constant (c) was doubled after the phase transformation. It also in turn proved that PBCMF-1 indeed had the layered structure, i.e., $[-\text{PrO}_x\text{-Mn}(\text{Fe})\text{O}_2\text{-Ba}(\text{Ca})\text{O-Mn}(\text{Fe})\text{O}_2\text{-PrO}_x-]$, along the c -axis.

The prepared double perovskite oxide demonstrated excellent activity toward oxygen catalysis in alkaline conditions. We initially performed ORR tests in O_2 -saturated 0.1 M KOH solutions. All the materials used in this study had roughly the same specific surface areas (see Table S3). Figure 2a compares the linear sweep voltammetry (LSV, 1600 rpm) plots of PBM, PBMF-0.5, PBMF-1, PBMF-1.5, and PBF. Albeit that the Mn-containing oxides generally exhibit good activity in ORR in alkaline conditions,¹ we observed that the partial substitution of Mn by Fe cations had altered the electrocatalytic activity of the double perovskite oxide. While both the onset potential (E_{onset}) and the half-wave potential ($E_{1/2}$) of PBMF-0.5 were essentially identical with those of PBM, these potentials clearly shifted positively when 50% of Mn was substituted by Fe (PBMF-1). E_{onset} reached 0.88 V vs RHE, whereas $E_{1/2}$ was up to 0.76 V vs RHE. However, further Fe doping decreased the performances to the contrast.

Figure 3. XPS spectra of (a) O 1s, (b) Fe 2p, and (c) Mn 2p profiles for the D-PBCMF-1 (cation-disordered) and PBCMF-1 (cation-ordered) samples.

Such an activity–composition correlation was investigated using a spectrum of techniques. The surface structure of the catalyst was revealed by X-ray photoelectron spectroscopy (XPS, Figure S3). The O 1s spectrum split into two doublets tentatively assigned to two species with discrepant ratios. The lower binding energy (BE) peaks usually correspond to the lattice oxygen, whereas the higher BE peaks are correlated with the adsorbed oxygen species. PBMF-1 has the highest proportion of adsorbed oxygen species among all the controls, presumably indicating its largest amount of surface oxygen defects. These surface oxygen defects have higher energy states and might be important active sites for ORR/OER.^{33,34} In addition to the oxygen defects, it is widely accepted that both the ORR and the OER catalytic activities of perovskite oxides are governed by the electronic structures of the transition metals in the B-sites. All the materials have redox couples in the B-sites, which are of much concern to electrocatalysis.^{11,35,36} More importantly, it has been confirmed that any perovskite oxide, with the σ^* -antibonding (e_g) orbital filling of the B-site transition metal close to unity, is expected to be a good ORR/OER catalyst.^{1,19} Since the electronic configurations of Fe and Mn, with similar e_g orbital fillings (determined by their valences and spin states), were confirmed for PBMF-0.5, PBMF-1, and PBMF-1.5 (Table S4 and Figure S3), it was not surprising to find that PBMF-1 had the highest electrochemical activity among the controls, since it showed the largest amount of surface oxygen defects. The prominent contributions of surface oxygen defects in ORR/OER are also widely reported elsewhere.^{16,17,37,38} Therefore, we confirmed that the non-stoichiometric oxygen (Table S5) and the surface oxygen defects (Table S4) are perhaps among the governing aspects affecting the ORR activity for the PBMF series.

After optimizing the composition of the B-site cation in the double perovskite (Mn/Fe = 1), we then examined the influence of the A-site dopant and the crystal structure on the ORR activity. Interestingly, when Ca was incorporated into the lattice, PBCMF-1 actually exhibited slightly improved ORR performance, topping all the perovskite controls (see Figure 2b and S4). The same effect of Ca-doping was attributable to the increased conductivity in the literature.³⁹ The phase transformation from D-PBCMF-1 to PBCMF-1 led to substantially enhanced ORR activity, plausibly being ascribed to the formed long-range ordered oxygen defect structure along with the enhanced electrical conductivity as shown elsewhere, including our previous work.^{16,30} Indeed, both the on-set and the half-wave potentials were still lower than those of the state-of-the-art Pt/C catalyst; they were comparable to the best alternatives

to date (see Table S6). More importantly, the substitution by Ca dramatically increased the chemical stability of the materials; more results and discussions are provided below. The kinetics of ORR were studied by varying the rotation rate in the LSV measurement (Figures 2c and S5). The sequentially obtained Koutechy–Levich plots (Figures 2c and S6) are all nearly linear, and the calculated numbers of electron-transferred for PBCMF-1 ranged from 4.1 to 4.3 at the selected voltages, indicating the approximate 4-electron reduction pathway.

In addition, PBCMF-1 demonstrates excellent performance for water oxidation in alkaline conditions, rendering great bifunctional activity in oxygen electrocatalysis (Figures 2d,e and S7). In Figure 2e, its OER overpotential (η) was 0.408 V vs RHE at 10 mA cm⁻² in Ar-saturated KOH, roughly the same with PBF and outperformed all the other controls including the classical Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) catalyst (η = 0.45 V vs RHE). Remarkably, its OER overpotential (η) was 0.40 V vs RHE at 10 mA cm⁻² in O₂-saturated KOH (Figure S7), identical to the performance in Ar-saturated KOH solution. Most of all, the OER activity of PBCMF-1 is comparable to that of some recently reported high-performance materials (see the η comparison in Table S7). This is logical since Fe-containing perovskites are usually good OER catalysts,^{1,18,37,40} and a moderate amount of iron-dopant could effectively promote the OER activity, assignable to its effect of stabilizing the metal cations at high oxidation state¹⁶ and tuning of the oxygen defects (*vide ante*).

To understand the doping effect that leads to the highest activity of PBCMF-1, we performed a series of analysis. PBCMF-1 had a fairly high concentration of surface oxygen defect according to the XPS spectra in Figure 3a (*vide supra*). The surface oxygen defects (both Adsorbed O and Adsorbed O') have higher energy states and are of much concern to oxygen catalysis. This observation is also consistent with the results of the temperature-programmed O₂-desorption analysis (O₂-TPD, Figure S8). Both PBCMF-1 and PBMF-1 exhibited several pronounced O₂ desorption peaks. The first peak below 500 °C belonged to the desorption of chemisorbed oxygen. PBCMF-1 processed a greater amount of adsorbed oxygen, suggesting more active sites for the adsorption of oxygen molecules. Another contributing factor comes from the intrinsic activity of Mn and Fe dopants. Both of them present e_g orbital fillings that are critical in oxygen electrocatalysis.¹ Figure 3b,c illustrates the Fe 2p and Mn 2p core-level spectra of PBCMF-1, which could be deconvoluted into several characteristic subpeaks of Mn²⁺/Mn³⁺/Mn⁴⁺ and Fe³⁺/Fe⁴⁺.^{41,42} The calculated average valences of Mn and Fe were 3.03 and 3.40,

Figure 4. (a) High-angle annular dark-field (HAADF) image and the corresponding elemental mappings of degraded PBMF-1 catalyst; Pr, Ba, Fe, Mn, and O are in dark cyan, pink, green, red, and yellow colors, respectively. (b) HRTEM micrograph and (c) a schematic of the near-surface structure of degraded PBMF-1.

Figure 5. (a) The formation energies of mobile oxygen species in the catalysts with different A-site dopants using DFT simulation. (b) The comparison of CV curves of PBCMF-1 catalyst in OER before and after 1000 cycles; the scan range is 0.2–0.8 V. vs Ag/AgCl with a 50 mV s⁻¹ scan rate. The near-surface region (c) HRTEM micrograph and (d) HAADF image and the corresponding elemental mappings of PBCMF-1 after the cycle test in OER; the inset is the bright-field image of the dashed square area. Pr, Ba, Fe, Mn, O, and Ca are in dark cyan, pink, green, red, yellow, and purple colors.

Figure 6. (a) Schematic of setup for *in situ* Raman spectroscopy. *In situ* Raman tests of (b) PBMF-1 and (c) PBCMF-1 in 10% CO₂-90% Air at 600 °C. *Ex situ* Raman tests of (d) PBMF-1 and (e) PBCMF-1 before and after OER stability test, showing the presence of –OH-containing species in Ca-free sample. These spectrum tests suggest the stability of PBMF-1 was enhanced by doping a small amount of Ca. (f) LSV curves of PBCMF-1 and Pt/C-RuO₂/C catalysts for ORR in O₂-saturated KOH before and after stability tests. (g) LSV curves of PBCMF-1 and Pt/C-RuO₂/C catalysts for OER in O₂-saturated KOH before and after stability tests. (The ORR stability test was performed at $E_{1/2}$ for 30 min, and then the OER stability test was performed at 10 mA cm^{−2} for 30 min. Such a cycling test has been repeated for 4 times.)

respectively, from which we can also calculate the $3-\delta$ value in PBCMF-1. It is found that the calculated $3-\delta$ value was in good agreement with the one obtained from the iodometric titration analysis (Table S5), which in turn proves that the e_g occupancies obtained from the XPS survey are reliable. The e_g occupancy of Mn in the PBCMF-1 catalyst is estimated to be 0.97 (close to unity), implying its good catalytic activity toward ORR/OER.^{1,19} Fe ions with high oxidation states (Fe⁴⁺) are generally preferred, as the e_g occupancy of Fe⁴⁺ is a unit of $t_{2g}^3 e_g^1$. In PBCMF-1, the ratio of Fe⁴⁺/Fe³⁺ is as high as 2/3, outperforming the well-designed La_{1-x}FeO_{3-δ} ORR/OER catalyst.³⁷

Notwithstanding the fact that both PBMF-1 and PBCMF-1 demonstrated superior performances in the chronoamperometric (Figure 2f–h) and 1000-cycle CV stability tests (Figure S9), the Ca-free counterpart, PBMF-1, suffered from an obvious degradation in the water oxidation reaction in particular. Its η increased dramatically from 0.42 to 0.47 V at 10 mA cm^{−2} after the 1000-cycle test. In fact, many well-known perovskite OER catalysts, such as BSCF^{28,29} and SrFeO_{3-δ} (SFO),⁴⁰ deteriorated gradually during water oxidation reaction, as surface amorphization and/or cation segregation occurred. To further understand the chemistry, we performed high-angle annular dark-field (HAADF) image and the corresponding energy-dispersive X-ray spectroscopic elemental mappings of the degraded PBMF-1 catalyst. A clear ~10 nm thick Ba-rich shell, the decomposition product, was identified on the surface in Figure 4a. The HRTEM image in Figure 4b reveals that the shell was majorly constituted of amorphous matters with embedded crystalline nanoparticles. Further TEM measurements implied that these crystals were likely the Fe- and Pr-containing compounds (see Figures S10 and S11). Therefore, a schematic of the near-surface structure of PBMF-1 after the stability test is drawn in Figure 4c. The high oxidation

potential along with the repeated redox cycle drives the surface decomposition of PBMF-1. The outmost surface was rich in A-site cations, forming an amorphous shell structure, while the layer beneath contained nanocrystals of B-site cations and probably formed a B-rich sublayer.^{43–45}

In theory, such a segregation effect could be caused by the significant cation-size mismatch of the dopant that reduces lattice stability.^{22,37} The electrostatic attraction of negatively charged A-site dopants (e.g., Ba_{A'}) toward a surface positively charged oxygen vacancies is another critical reason behind the cation surface enrichment.^{22,25} Therefore, before the selection of the dopant, we first employ the first-principles density functional theory (DFT) calculations to determine the influence of various dopants over the stability of mobile oxygen (O*) in the PBMF-1 double perovskite. According to the XRD and TEM analysis, we constructed the model by using a tetragonal symmetry ($P4/nmm$, $a = b = 3.95$, $c = 7.86$). The formation energy of O* is defined in eq 1.

$$E_f(O^*) = E_{\text{tot}}(O_6) - E_{\text{tot}}(O_5) - N\mu_0 \quad (1)$$

in which $E_{\text{tot}}(O_6)$ and $E_{\text{tot}}(O_5)$ are the total energies of systems with and without O*, respectively, N is the number of O* in the unit cell, and μ_0 is the chemical potential of an O atom. The calculation result in Figure 5a suggests that, among Ba, Sr, and Ca, Ca is the optimum dopant which can effectively enhance the stability of O* in PBCMF-1. Consequently, the enhanced stability of O* in the bulks contributed to the enhancement of the chemical-electrochemical stability of PBCMF-1. In the chronoamperometric tests, the degradation rate of ORR $E_{1/2}$ was merely 0.67 mV/h, while the rate of OER potential loss at 10 mA cm^{−2} was only 0.75 mV/h (Figure 2f–h). Besides, no apparent overpotential change was found after the 1000-cycle OER test in Figure 5b (see also Figure S10).

The tested PBCMF-1 was also examined via TEM analysis. The HRTEM micrograph in Figure 5c presents the well-resolved crystal lattice near the surface, substantiating the robustness of the material. The HAADF image and the corresponding elemental mappings in Figure 5d show that all the elements were uniformly distributed across the entire region without segregating on the surface (cf. the TEM results in Figure 4). In fact, the TGA results in Figure S2 also proved the enhanced structural stability of PBCMF-1: The substitution of Ca rendered a remarkably extended temperature region of stability in H₂ without being decomposed.

To further elucidate the superior stability of the Ca doped sample, *in situ* and *ex situ* Raman spectroscopy have been employed to compare the behaviors of catalysts. Traditionally, Ba-containing perovskite oxides have been proven susceptible to the presence of CO₂. The deteriorations of the oxygen catalytic activity and oxygen permeability upon the exposure to CO₂ have been widely reported.²² The decomposition of perovskite oxide in the gas phase follows a similar way to that in liquids. We first performed *in situ* time-resolved Raman at 600 °C in a mixed gas (10% CO₂-90% Air) to *in situ* observe the accelerated deterioration of the catalysts. The setup is depicted in Figure 6a. A strong peak at 1060 cm⁻¹ emerged on the PBMF-1 sample during the CO₂ tolerance test, suggesting the presence of carbonate (–CO₃) species (Figure 6b). Conversely, there is no obvious change in the Raman curves of the PBCMF-1 sample, and in turn they demonstrated its superior CO₂ tolerance (Figure 6c). The *ex situ* Raman spectroscopy was also employed to study the used catalyst after the electrochemical tests. Figure 6d reveals a strong –OH species in the PBMF-1 sample after 1000 cycles of the CV stability test, pertaining to its surface amorphization. In contrast, no appreciable peaks have been detected in the PBCMF-1 sample (Figure 6e). These results proved that the stability of PBMF-1 was enhanced by doping a small amount of Ca cations at the A-site.

Finally, we have drawn a comparison between our catalyst and commercial Pt/C-RuO₂/C catalyst with respect to the bifunctional activity and durability. The electrodes were first polarized in ORR at E_{1/2} for 30 min. Then, the polarization potentials were extended to the OER region while ensuring a constant current density of 10 mA cm⁻² for 30 min. Panels (f) and (g) in Figure 6 compare the LSV curves of PBCMF-1 and Pt/C-RuO₂/C catalysts before and after 4 ORR-OER cycling tests. Remarkably, compared to the well-known commercial catalyst, the PBCMF-1 exhibited matchable catalytic activity and better stability in regards to the bifunctional oxygen catalysis.

3. CONCLUSIONS

In this work, we showed that the cobalt-free double perovskite oxide, PrBa_{0.85}Ca_{0.15}MnFeO_{5+δ}, had excellent ORR/OER catalytic activity and structural stability in alkaline conditions. The sandwich-like crystal structure provided long-range ordered oxygen vacancies, and the moderate amount of iron doping stabilized the metal cations at high oxidation state with a large amount of surface oxygen species and optimal e_g fillings. Both of them contributed to a high ORR E_{1/2} of 0.77 V and a low OER potential of 1.64 V at 10 mA cm⁻². Besides, on the basis of the computational simulation, we experimentally showed that the Ca substitution successfully reinforced the perovskite structure, preventing the surface degradation (cation segregation and amorphization), and thus rendered excellent stability in oxygen electrocatalytic reactions.

4. EXPERIMENTAL SECTION

4.1. Powder Preparations. To prepare the (PrBa_{0.85}Ca_{0.15})_{0.5}–(MnFe)_{0.5}O_{3–δ} (D-PBCMF-1) powder, stoichiometric amounts of the nitrates were dissolved in the distilled water with the ethylene glycol and the citric acid as the chelant agents. The solution was vaporized on a hot plate. Then, it was heated in an oven at 300 °C to form the precursor. The precursor was fired in air and at 900 °C for 5 h to form the D-PBCMF-1 perovskite oxide. The same procedure was adopted to prepare the PrBaFe₂O_{5+δ} (PBF), Pr_{0.5}Ba_{0.5}MnO_{3–δ} (D-PBM), Pr_{0.5}Ba_{0.5}Mn_{0.75}Fe_{0.25}O_{3–δ} (D-PBMF-0.5), Pr_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3–δ} (D-PBMF-1), PrBaMn_{0.5}Fe_{1.5}O_{5+δ} (PBMF-1.5), and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3–δ} (BSCF) powders. The ordered PBF and PBMF-1.5 samples were directly obtained in air. Instead, the cation ordered PrBaMn₂O_{5+δ} (PBM), PrBaMnFeO_{5+δ} (PBMF-1), PrBaMn_{1.5}Fe_{0.5}O_{5+δ} (PBMF-0.5), and PrBa_{0.85}Ca_{0.15}MnFeO_{5+δ} (PBCMF-1) were obtained by reducing the D-PBM, D-PBMF-1, D-PBMF-0.5, and D-PBCMF-1, in 5% H₂-95% N₂ and at 600 °C for 4 h, respectively. In order to keep consistent, the same heat treatments were also performed for the PBF and PBMF-1.5. The catalysts in this study are summarized in Table S1.

4.2. Preparation of the Electrodes. For the ORR/OER (oxygen reduction reaction/oxygen evolution reaction) tests, the catalyst membranes were prepared using a refined slurry coating technology. Initially, 10 mg of catalyst powder was physically mixed with 10 mg of carbon black (Cabot). Then, 0.2 mL of Nafion solution (5 wt %, Aldrich) and 0.8 mL of isopropyl alcohol solution (Fisher Scientific) were added, followed by ultrasonication for 1 h in order to form homogeneous ink. 5.5 μL of the catalyst ink was dropped onto a polished glassy carbon (GC) electrode of 5 mm in diameter (Glassy Carbon Rotating Disk Electrode, RDE tip, Model. AFEST050GC, Pine Research Instrumentation). The catalyst-coated GC electrode was then dried at room temperature for 1 h. The area of the electrode is 0.196 cm² with a mass load of 0.2806 mg cm⁻² (perovskite oxide). We also tested a commercial Pt/C catalyst (20 wt % Pt Vulcan carbon, Sigma-Aldrich) with a mass load of 0.1122 mg/cm² (Pt metal) for comparison. The mass load of Pt/C is 0.5612 mg cm⁻². Besides, we tested a carbon black samples for comparison. The mass load of carbon black is 0.5612 mg cm⁻².

4.3. Electrochemical Tests. The half-cell experiment for ORR was carried out using a three-electrode method. A catalyst coated glassy carbon RDE tip was used as working electrode, while Pt wire and Ag/AgCl/1.0 M KOH were used as the counter electrode and reference electrode, respectively. 0.10 M KOH was used as electrolyte. Pure oxygen gas (99.9%) was purged for 30 min before RDE experiment to make the electrolyte saturated with oxygen. The electrochemical characterizations of the catalysts were conducted using the Solartron 1255+1287 with a scan rate of 20 mV s⁻¹ at 400, 900, 1600, and 2500 rpm. The ORR mechanism was further examined using the Koutecky–Levich correlations to obtain the electron transfer number (*n*) in ORR. The K-L plots were drawn according to the following equations

$$\frac{1}{J_d} = \frac{1}{J_k} + \frac{1}{J_{dl}} \quad (2)$$

$$J_k = nFAkC_{O_2} \quad (3)$$

$$J_{dl} = 0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6}\omega^{1/2} = B\omega^{1/2} \quad (4)$$

$$B = 0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6} \quad (5)$$

$$\frac{1}{J_d} = \frac{1}{J_k} + \frac{1}{J_{dl}} = \frac{1}{J_k} + \frac{1}{B}\omega^{-1/2} \quad (6)$$

J_d, *J_k*, and *J_{dl}* are the tested disk current density, kinetic current density, and film diffusion limiting current density, respectively. *F* is the Faraday constant (96500 C mol⁻¹), *A* is the area of the RDE tip (0.196 cm²), *C_{O₂}* is the oxygen concentration in 0.1 M KOH (1.14 × 10⁻⁶ mol cm⁻³), *D_{O₂}* is the oxygen diffusion coefficient in 0.1 M KOH (1.73 × 10⁻⁵ cm² s⁻¹), *ν* is the kinematic viscosity of the 0.1 M KOH

solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$), ω is the electrode rotation rate (rpm), and k is the electron transfer rate constant for the ORR. The ORR stability test was performed at a constant potential (e.g., initial $E_{1/2}$).

The half-cell experiment for OER was also carried out using a three-electrode method. A catalyst coated glassy carbon RDE tip was used as working electrode, while Pt wire and Ag/AgCl/1.0 M KOH were used as the counter electrode and reference electrode, respectively. 0.10 M KOH was used as electrolyte. Pure argon gas (99.9%) or pure oxygen gas (99.9%) was purged for 30 min before RDE experiment to make the electrolyte saturated with argon or oxygen. Electrochemical characterizations of the catalysts were conducted using a Solartron 1255+1287 with a scan rate of 20 mV s^{-1} at 1600 rpm. The OER stability test was performed at a constant potential to ensure the initial current density of 5 mA cm^{-2} .

4.4. Computational Calculations. The density functional theory (DFT) calculations were performed by using the Projector Augmented Wave (PAW) pseudo potentials as implemented in the Vienna Ab initio Simulation Package (VASP). The exchange correlation functional was treated within the Generalized Gradient Approximation (GGA) and parametrized by the Perdew–Burke–Ernzerhof (PBE) formula. The Brillouin-zone integrations were approximated by using the special k -point sampling of the Monkhorst–Pack scheme. A cutoff energy of 600 eV and a mesh size of $8 \times 8 \times 8$ were used for geometry optimization and electronic property calculations. Utilizing the block Davidson scheme, both the atomic positions and cell parameters were optimized to the level of the residual forces below $10^{-5} \text{ eV \AA}^{-1}$. The formation energy of mobile oxygen (O^*) is defined in eq 1.

4.5. Characterizations. The powder materials were subjected to the X-ray diffraction analysis (Rigaku Rotaflex) using Cu K α radiation generated at 40 kV and 44 mA. During the test, the scan rate was 1° min^{-1} and the 2θ range was ranging from 20° to 80° .

A suitable amount of the powder was loaded to an alumina microcrucible in the SDT-Q600 (TA Instruments, USA) apparatus to conduct the TGA analysis. The heating rate was $2^\circ \text{C min}^{-1}$ or $20^\circ \text{C min}^{-1}$. The gas environment was selected as 5% H_2 balanced by N_2 .

Transmission electron microscope analysis of various samples was performed using a Hitachi H-9500 environmental transmission electron microscope (ETEM) with a 100 kV accelerating voltage and a FEI's Tecnai Osiris TEM equipped with X-FEG gun at 200 keV.

X-ray photoelectron spectroscopy (XPS, Kratos AXIS) was carried out to examine the surface chemistry of the sample. A monochromatic Al K α source ($h\nu = 1486.6 \text{ eV}$) was used with a power of 210 W and a base pressure of $3 \times 10^{-8} \text{ Pa}$ in the analytical chamber. Spectra were referenced to the C 1s binding energy of 284.6 eV and fitted using Gaussian–Lorentzian peak shapes and Shirley baselines.

The Brunauer–Emmett–Teller (BET) specific surface areas of various catalysts were measured by the N_2 adsorption/desorption method using an Autosorb Quantachrome 1MP apparatus.

Raman characterization was performed using Renishaw R1000 and Dilor LabRam I microprobe Raman systems. The excitation wavelength was a 532 nm He–Cd laser with a power of $\sim 3 \text{ mW}$ at the analysis spot. The samples were loaded in the *in situ* chamber in the test atmosphere and temperature. *Ex situ* Raman analysis of PBMF-1 and PBCMF-1 before and after electrochemical test was also performed.

Temperature-programmed desorption (TPD) was carried out using a home-built temperature-programmed apparatus. The sample was first treated in Ar at 500°C for 1 h to remove all the adsorbed species before cooling down to room temperature. Then, it was exposed to O_2 for 2 h. After purging the analysis chamber with Ar for 1 h at room temperature, the system was heated up to 900°C in the stream of Ar. The released O_2 was monitored and recorded continuously as a function of the temperature by the QIC-20 detector (Atmospheric Gas Analysis System).

The oxygen content ($3-\delta$) of the perovskite at room temperature was determined using the iodometric titration method. 20 mg of powder was placed in an Erlenmeyer flask, followed by adding a small amount of 2 M KI solution. Then, 3.5 M HCl was added to completely dissolve the powders. During this process, a stream of N_2 flow was

used to blanket the solution. The clear solution was titrated with a 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as the indicator.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.7b01114](https://doi.org/10.1021/acs.chemmater.7b01114).

XRD patterns of various perovskites; TGA tests of PBCFM-1 and PBMF-1 in 10% H_2 -90% N_2 ; XPS analysis of PBMF-1.5, PBMF-1, PBMF-0.5; LSV and K-L plots for various catalysts; O_2 -TPD tests of PBCMF-1 and PBMF-1 powders; TEM and SEM images for the powders (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Chen, D.; Chen, C.; Baiye, Z. M.; Shao, Z.; Ciucci, F. Nonstoichiometric Oxides as Low-Cost and Highly-Efficient Oxygen Reduction/Evolution Catalysts for Low-Temperature Electrochemical Devices. *Chem. Rev.* **2015**, *115*, 9869–9921.
- (2) Mefford, J. T.; Rong, X.; Abakumov, A. M.; Hardin, W. G.; Dai, S.; Kolpak, A. M.; Johnston, K. P.; Stevenson, K. J. Water electrolysis on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ perovskite electrocatalysts. *Nat. Commun.* **2016**, *7*, 11053.
- (3) Zhao, B.; Zhang, L.; Zhen, D.; Yoo, S.; Ding, Y.; Chen, D.; Chen, Y.; Zhang, Q.; Doyle, B.; Xiong, X.; Liu, M. A tailored double perovskite nanofiber catalyst enables ultrafast oxygen evolution. *Nat. Commun.* **2017**, *8*, 14586.
- (4) Lee, D. U.; Xu, P.; Cano, Z. P.; Kashkooli, A. G.; Park, M. G.; Chen, Z. Recent progress and perspectives on bi-functional oxygen electrocatalysts for advanced rechargeable metal-air batteries. *J. Mater. Chem. A* **2016**, *4*, 7107–7134.
- (5) Su, C.; Wang, W.; Liu, M.; Tadé, M. O.; Shao, Z. Progress and Prospects in Symmetrical Solid Oxide Fuel Cells with Two Identical Electrodes. *Adv. Energy Mater.* **2015**, *5*, 1500188.
- (6) Chen, Y.; Zhou, W.; Ding, D.; Liu, M.; Ciucci, F.; Tade, M.; Shao, Z. Advances in Cathode Materials for Solid Oxide Fuel Cells: Complex Oxides without Alkaline Earth Metal Elements. *Adv. Energy Mater.* **2015**, *5*, 1500537.
- (7) Holewinski, A.; Idrobo, J.-C.; Linic, S. High-performance Ag–Co alloy catalysts for electrochemical oxygen reduction. *Nat. Chem.* **2014**, *6*, 828–834.
- (8) Ng, J. W. D.; García-Melchor, M.; Bajdich, M.; Chakthranont, P.; Kirk, C.; Vojvodica, A.; Jaramillo, T. F. Gold-supported cerium-doped NiOx catalysts for water oxidation. *Nat. Energy* **2016**, *1*, 16053.

- (9) Du, X. X.; He, Y.; Wang, X. X.; Wang, J. N. Fine-grained and fully ordered intermetallic PtFe catalysts with largely enhanced catalytic activity and durability. *Energy Environ. Sci.* **2016**, *9*, 2623–2632.
- (10) Zhu, Y.; Zhou, W.; Sunarso, J.; Zhong, Y.; Shao, Z. Phosphorus-Doped Perovskite Oxide as Highly Efficient Water Oxidation Electrocatalyst in Alkaline Solution. *Adv. Funct. Mater.* **2016**, *26*, 5862–5872.
- (11) Shao, M.; Chang, Q.; Dodelet, J. P.; Chenitz, R. Recent Advances in Electrocatalysts for Oxygen Reduction Reaction. *Chem. Rev.* **2016**, *116*, 3594–657.
- (12) Li, X.; Hao, X.; Abudula, A.; Guan, G. Nanostructured catalysts for electrochemical water splitting: current state and prospects. *J. Mater. Chem. A* **2016**, *4*, 11973–12000.
- (13) Zhang, Z.; Luo, Z.; Chen, B.; Wei, C.; Zhao, J.; Chen, J.; Zhang, X.; Lai, Z.; Fan, Z.; Tan, C.; Zhao, M.; Lu, Q.; Li, B.; Zong, Y.; Yan, C.; Wang, G.; Xu, Z. J.; Zhang, H. One-Pot Synthesis of Highly Anisotropic Five-Fold-Twinned PtCu Nanoframes Used as a Bifunctional Electrocatalyst for Oxygen Reduction and Methanol Oxidation. *Adv. Mater.* **2016**, *28*, 8712–8717.
- (14) Jung, J.-I.; Risch, M.; Park, S.; Kim, M. G.; Nam, G.; Jeong, H.-Y.; Shao-Horn, Y.; Cho, J. Optimizing nanoparticle perovskite for bifunctional oxygen electrocatalysis. *Energy Environ. Sci.* **2016**, *9*, 176–183.
- (15) Zhou, W.; Zhao, M.; Liang, F.; Smith, S. C.; Zhu, Z. High activity and durability of novel perovskite electrocatalysts for water oxidation. *Mater. Horiz.* **2015**, *2*, 495–501.
- (16) Hua, B.; Zhang, Y.-Q.; Yan, N.; Li, M.; Sun, Y.-F.; Chen, J.; Li, J.; Luo, J.-L. The Excellence of Both Worlds: Developing Effective Double Perovskite Oxide Catalyst of Oxygen Reduction Reaction for Room and Elevated Temperature Applications. *Adv. Funct. Mater.* **2016**, *26*, 4106–4112.
- (17) Xu, X.; Chen, Y.; Zhou, W.; Zhu, Z.; Su, C.; Liu, M.; Shao, Z. A Perovskite Electrocatalyst for Efficient Hydrogen Evolution Reaction. *Adv. Mater.* **2016**, *28*, 6442–6448.
- (18) Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y. L.; Risch, M.; Hong, W. T.; Zhou, J.; Shao-Horn, Y. Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution. *Nat. Commun.* **2013**, *4*, 2439.
- (19) Hong, W. T.; Risch, M.; Stoerzinger, K. A.; Grimaud, A.; Suntivich, J.; Shao-Horn, Y. Toward the rational design of non-precious transition metal oxides for oxygen electrocatalysis. *Energy Environ. Sci.* **2015**, *8*, 1404–1427.
- (20) Yoo, S.; Jun, A.; Ju, Y. W.; Odhhuu, D.; Hyodo, J.; Jeong, H. Y.; Park, N.; Shin, J.; Ishihara, T.; Kim, G. Development of double-perovskite compounds as cathode materials for low-temperature solid oxide fuel cells. *Angew. Chem., Int. Ed.* **2014**, *53*, 13064–13067.
- (21) Azizi, F.; Kahoul, A.; Azizi, A. Effect of La doping on the electrochemical activity of double perovskite oxide $\text{Sr}_2\text{FeMoO}_6$ in alkaline medium. *J. Alloys Compd.* **2009**, *484*, 555–560.
- (22) Tsvetkov, N.; Lu, Q.; Sun, L.; Crumlin, E. J.; Yildiz, B. Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface. *Nat. Mater.* **2016**, *15*, 1010–1016.
- (23) Han, B.; Risch, M.; Lee, Y.-L.; Ling, C.; Jia, H.; Shao-Horn, Y. Activity and stability trends of perovskite oxides for oxygen evolution catalysis at neutral pH. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22576–22580.
- (24) Irvine, J. T. S.; Neagu, D.; Verbraeken, M. C.; Chatzichristodoulou, C.; Graves, C.; Mogensen, M. B. Evolution of the electrochemical interface in high-temperature fuel cells and electrolyzers. *Nat. Energy* **2016**, *1*, 15014.
- (25) Lee, W.; Han, J. W.; Chen, Y.; Cai, Z.; Yildiz, B. Cation size mismatch and charge interactions drive dopant segregation at the surfaces of Manganite perovskites. *J. Am. Chem. Soc.* **2013**, *135*, 7909–7925.
- (26) Jung, W.; Tuller, H. L. Investigation of surface Sr segregation in model thin film solid oxide fuel cell perovskite electrodes. *Energy Environ. Sci.* **2012**, *5*, 5370–5378.
- (27) Jun, A.; Kim, J.; Shin, J.; Kim, G. Perovskite as a Cathode Material: A Review of its Role in Solid-Oxide Fuel Cell Technology. *ChemElectroChem* **2016**, *3*, 511–530.
- (28) Risch, M.; Grimaud, A.; May, K. J.; Stoerzinger, K. A.; Chen, T. J.; Mansour, A. N.; Shao-Horn, Y. Structural Changes of Cobalt-Based Perovskites upon Water Oxidation Investigated by EXAFS. *J. Phys. Chem. C* **2013**, *117*, 8628–8635.
- (29) May, K. J.; Carlton, C. E.; Stoerzinger, K. A.; Risch, M.; Suntivich, J.; Lee, Y.-L.; Grimaud, A.; Shao-Horn, Y. Influence of Oxygen Evolution during Water Oxidation on the Surface of Perovskite Oxide Catalysts. *J. Phys. Chem. Lett.* **2012**, *3*, 3264–3270.
- (30) Sengodan, S.; Choi, S.; Jun, A.; Shin, T. H.; Ju, Y.-W.; Jeong, H. Y.; Shin, J.; Irvine, J. T. S.; Kim, G. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. *Nat. Mater.* **2015**, *14*, 205–209.
- (31) Sun, Y. F.; Zhang, Y. Q.; Chen, J.; Li, J. H.; Zhu, Y. T.; Zeng, Y. M.; Amirkhiz, B. S.; Li, J.; Hua, B.; Luo, J. L. New Opportunity for in Situ Exsolution of Metallic Nanoparticles on Perovskite Parent. *Nano Lett.* **2016**, *16*, 5303–5309.
- (32) Munoz-Gil, D.; Avila-Brandé, D.; Urones-Garrote, E.; Garcia-Martin, S. Ordering effects in the crystal structure and electrochemical properties of the $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ perovskite. *Dalton Trans.* **2015**, *44*, 10867–10874.
- (33) Ma, T. Y.; Zheng, Y.; Dai, S.; Jaroniec, M.; Qiao, S. Z. Mesoporous MnCo_2O_4 with abundant oxygen vacancy defects as high-performance oxygen reduction catalysts. *J. Mater. Chem. A* **2014**, *2*, 8676–8682.
- (34) Grimaud, A.; Diaz-Morales, O.; Han, B.; Hong, W. T.; Lee, Y.-L.; Giordano, L.; Stoerzinger, K. A.; Koper, M. T. M.; Shao-Horn, Y. Activating lattice oxygen redox reactions in metal oxides to catalyze oxygen evolution. *Nat. Chem.* **2017**, *9*, 457–465.
- (35) Liu, Y.; Cao, L.-J.; Cao, C.-W.; Wang, M.; Leung, K.-L.; Zeng, S.-S.; Hung, T. F.; Chung, C. Y.; Lu, Z.-G. Facile synthesis of spinel CuCo_2O_4 nanocrystals as high-performance cathode catalysts for rechargeable Li–air batteries. *Chem. Commun.* **2014**, *50*, 14635–14638.
- (36) Liu, Y.; Liu, Y.; Shi, H.; Wang, M.; Cheng, S. H.-S.; Bian, H.; Kamruzzaman, M.; Cao, L.; Chung, C. Y.; Lu, Z. Cobalt-copper layered double hydroxide nanosheets as high performance bifunctional catalysts for rechargeable lithium-air batteries. *J. Alloys Compd.* **2016**, *688*, 380–387.
- (37) Zhu, Y.; Zhou, W.; Yu, J.; Chen, Y.; Liu, M.; Shao, Z. Enhancing Electrocatalytic Activity of Perovskite Oxides by Tuning Cation Deficiency for Oxygen Reduction and Evolution Reactions. *Chem. Mater.* **2016**, *28*, 1691–1697.
- (38) Jung, J.-I.; Park, S.; Kim, M.-G.; Cho, J. Tunable Internal and Surface Structures of the Bifunctional Oxygen Perovskite Catalysts. *Adv. Energy Mater.* **2015**, *5*, 1501560.
- (39) Choi, S.; Park, S.; Shin, J.; Kim, G. The effect of calcium doping on the improvement of performance and durability in a layered perovskite cathode for intermediate-temperature solid oxide fuel cells. *J. Mater. Chem. A* **2015**, *3*, 6088–6095.
- (40) Yagi, S.; Yamada, I.; Tsukasaki, H.; Seno, A.; Murakami, M.; Fujii, H.; Chen, H.; Umezawa, N.; Abe, H.; Nishiyama, N.; Mori, S. Covalency-reinforced oxygen evolution reaction catalyst. *Nat. Commun.* **2015**, *6*, 8249.
- (41) Jin, F.; Shen, Y.; Wang, R.; He, T. Double-perovskite $\text{PrBaCo}_{2/3}\text{Fe}_{2/3}\text{Cu}_{2/3}\text{O}_{5+\delta}$ as cathode material for intermediate-temperature solid-oxide fuel cells. *J. Power Sources* **2013**, *234*, 244.
- (42) Yatsunami, T.; Takase, S.; Shimizu, Y. Amperometric Nitrite-Ion Sensor Based on Electrodeposited Sm-Based Perovskite-Type Oxide Thick-Film Electrode. *Sensors Mater.* **2016**, *28*, 777–784.
- (43) Druce, J.; Tellez, H.; Burriel, M.; Sharp, M. D.; Fawcett, L. J.; Cook, S. N.; McPhail, D. S.; Ishihara, T.; Brongersma, H. H.; Kilner, J. A. Surface termination and subsurface restructuring of perovskite-based solid oxide electrode materials. *Energy Environ. Sci.* **2014**, *7*, 3593–3599.

- (44) Wu, J.; Pramana, S. S.; Skinner, S. J.; Kilner, J. A.; Horsfield, A. P. Why Ni is absent from the surface of $\text{La}_2\text{NiO}_{4+\delta}$. *J. Mater. Chem. A* **2015**, 3, 23760–23767.
- (45) Kim, J.-H.; Manthiram, A. Layered $\text{LnBaCo}_2\text{O}_{5+\delta}$ perovskite cathodes for solid oxide fuel cells: an overview and perspective. *J. Mater. Chem. A* **2015**, 3, 24195–24210.