Fe-Doping in Double Perovskite PrBaCo$_{2(1-x)}$Fe$_{2x}$O$_6$: Insights into Structural and Electronic Effects to Enhance Oxygen Evolution Catalyst Stability

Kim, Bae-Jung; Fabbri, Emiliana; Castelli, Ivano E.; Borlaf, Mario; Graule, Thomas; Nachtegaal, Maarten; Schmidt, Thomas J.

Published in:
Catalysts

Link to article, DOI:
10.3390/catal9030263

Publication date:
2019

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Fe-Doping in Double Perovskite PrBaCo$_2$(1-x)Fe$_2$xO$_6$$\delta$:
Insights into Structural and Electronic Effects to Enhance Oxygen Evolution Catalyst Stability

Bae-Jung Kim 1,*, Emiliana Fabbri 1,*, Ivano E. Castelli 2, Mario Borlaf 3, Thomas Graule 3,
Maarten Nachtegaal 1, Thomas J. Schmidt 1,4

1 Paul Scherrer Institut, Forschungstrasse 111, 5232 Villigen PSI, Switzerland
2 Department of Energy Conversion and Storage, Fysikvej 309, Technical University of Denmark, DK-2800, Kgs. Lyngby, Denmark; ivca@dtu.dk
3 Laboratory for High Performance Ceramics, Empa, Swiss Federal Laboratories for Materials Testing and Research, 8600 Dübendorf, Switzerland; mario.borlaf@empa.ch, thomas.graule@empa.ch
4 Laboratory of Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland; thomasjustus.schmidt@psi.ch

* Correspondence: Baejung Kim joseph.kim@psi.ch; Tel.: +41-56-310-4580; Emiliana Fabbri emiliana.fabbri@psi.ch; Tel.: +41-56-310-2795

Received: date; Accepted: date; Published: date

Abstract: Perovskite oxides have been gaining attention for their capability to be designed as an ideal electrocatalyst for oxygen evolution reaction (OER). Among promising candidates, the layered double perovskite – PrBaCo$_2$O$_6$ (PBC) – has been identified as the most active perovskite electrocatalyst for OER in alkaline media. For a single transition metal oxide catalyst, the addition of Fe enhances its electrocatalytic performance towards OER. To understand the role of Fe, herein, Fe is incorporated in PBC in different ratios, which yielded PrBaCo$_2$(1-x)Fe$_2$xCo$_6$ (x = 0, 0.2 and 0.5). Fe-doped PBC’s demonstrate enhanced OER activities and stabilities. Operando X-ray absorption spectroscopy (XAS) revealed that Co is more stable in a lower oxidation state upon Fe incorporation by establishing charge stability. Hence, as degradation of Co is inhibited such that the perovskite structure is prolonged under the OER conditions being able to serve as platform for the oxy(hydroxide) layer formation. Overall, our findings underline synergetic effects of incorporating Fe into Co-based layered double perovskite in achieving a higher oxygen evolution reaction activity and stability.

Keywords: Fe-doping; operando X-ray absorption spectroscopy; oxygen evolution reaction; layered double perovskite catalysts; water splitting

1. Introduction

Today modern society is evolving to become more energy dependent. As the awareness of environmental impact from current energy systems is elevating, more efforts have recently been devoted towards mainstreaming renewable energy sources. However, the implementation of renewable energy technologies is challenging as it requires an efficient energy storage system to mediate the intermittent generation and consumption of energy. The electrochemical splitting of water (i.e. water electrolysis) offers an effective method to produce large amounts of hydrogen (H$_2$), which can be stored as an energy vector.[1] Therefore, an efficient oxygen evolution reaction (OER) is essential as it is the key reaction in water electrolysis. During the past decade, the members of the perovskite oxide family (ABO$_3$) have been gaining vast attention for their promising activities as OER electrocatalysts under alkaline conditions, and thereby relieving the need of expensive precious metals such as iridium.[2-7] Principally, perovskite oxides are composed of rare-earth (e.g.
lantanides) or earth alkaline metals (e.g. Ba) in the A-site and 3d transition metals in the B-site (e.g. Ni, Co and/or Fe). The perovskites intrinsic properties can be tailored through partial cation substitution.[2,8,9] This substitution can transpire in both A- and B-sites of the perovskite (i.e. \(A'^{+}\) \(\rightarrow\) \(A''^{+}\), \(B'^{2-}\) \(\rightarrow\) \(B''^{2-}\); \(0 \leq n, m \leq 1\)) either in ordered or random arrangement.[10] Likewise, cation ordering plays an important role in engineering the intrinsic properties of a perovskite such as electronic structure, ionic conductivity, and magnetic properties; all of which may change its electrocatalytic behavior.[3,10,11] The recently proposed OER mechanism[12,13] emphasizes that the formation of oxy(hydroxide) at the metal oxide surface is vital along the path of lattice oxygen evolution reaction (LOER). In this context, developing perovskite oxides as the catalyst is advantageous owing to its ability to exhibit high oxygen vacancy concentration upon cation substitution and ordering as to activate the LOER.[14,15] The oxygen vacancy can create Unlike in the conventional OER mechanism,[16,17] in the case when the lattice oxygen is directly involved (i.e. LOER), the high surface OH coverage from the alkaline media is no longer necessary as loosely bonded lattice oxygen atoms act as the reaction intermediates itself; as a result, the overpotential is lowered.[12,18] In this regard, the use of layered double perovskite oxides \((A'_{2x}A''_{2y}B'_{2z}B''_{2w}O_{x+y}; 0 \leq n, m \leq 1)\) is beneficial as they tend to localize the oxygen vacancies also into layers through A-site ordering and promotes high oxygen mobility.[14] Among the layered double perovskite family, \(PrBaCoO_{6.5}\) (PBC) has been appraised for its high OER activity.[19-25] Nevertheless, past studies \([2,13,24,26-28]\) point out the instability of PBC under OER conditions, raising queries regarding its degradation mechanism. In our recent study,[2] we highlighted that the degradation is a kinetic process and every catalyst varies in how it reaches the end of its service life depending on the inherent properties.

In a different perspective, a single randomly-ordered perovskite oxide, \(Ba_{0.5Sr_{0.5}Co_{0.5}Fe_{0.5}O_{3.5}}\) (BSCF), has been identified as one of the most active OER catalyst.[23,29-31] More recently, we have reported that highly oxygen deficient BSCF prepared via flame spray synthesis would lead to the participation of lattice oxygen atoms (i.e. LOER) coupled with the OER process. Based on operando X-ray absorption spectroscopy (XAS) results[2,25,30] and density-functional theory (DFT) based calculations[2,25], BSCF exhibits the capability to facilitate the formation of a self-constructed oxy(hydroxide) surface layer during OER, owing to its thermodynamic nature of meta-stability under the OER condition. Intriguingly, in the means to understand each individual chemical component of BSCF, recent findings highlight the vital role of Fe in its B-site as to maintain the thermodynamic meta-stability, and provide charge stability.[25] Likewise, many studies have reported constructive effect of incorporating Fe into 3d transition metal oxide catalysts for OER.[32-41]

Therefore, in this study, we incorporate Fe into the B-site of PBC in different ratios to yield \(PrBaCo_{2(1-x)}Fe_xCo_{0.5}\) \((x = 0.2, 0.5;\) denoted as PBCF82 and PBCF55, respectively) for the purpose of tailoring the electrocatalytic performance with respect to OER activity and stability. Nanoparticles of all the materials under study are attained via flame spray synthesis.[42] Operando XAS is used to gain insights into the changes in local electronic and geometric structures of the layered double perovskites upon Fe-doping. Combined with the thermodynamic nature inferred from DFT calculations, the roles of Fe in the layered double perovskite as OER catalyst are highlighted. Based on our findings, we underline the synergetic effect that Fe conveys and elucidate the enhanced OER performance of layered double perovskite catalyst upon Fe incorporation.

2. Results and Discussion

2.1. Physical Characterization

All perovskite catalysts – \(PrBaCo_{2(1-x)}Fe_xCo_{0.5}\) \((x = 0, 0.2, \) and 0.5; denoted as PBC, PBCF82, and PBCF55, respectively) – are prepared via flame spray synthesis from which nano-scaled particles are obtained (Figure 1). Metal precursors are dissolved in combustible solution and injected into the flame at high temperature (possible up to \(\sim 3000 \text{ °C}\)) and the resulting precipitates are collected. Previously, we have established the benefits of this particular synthesis of perovskites for the electrocatalytic performance.[2,30] The physical and structural traits of such nanoparticles are observed using transmission electron microscopy (TEM) (Figure 1). Figure 1a, b, and c show the TEM
images of the prepared nanoparticles of PBC, PBCF82, and PBCF55, respectively. All of the prepared nanoparticles are in sizes that range from 5 – 30 nm. Each inset of Figure 1a, b, and c shows high-resolution (HR) TEM images of PBC, PBCF82, and PBCF55, respectively, and each reveals clear fringes indicating the formation of crystalline structures.

**Figure 1.** Transmission electron microscopy (TEM) images of (a) PBC, (b) PBCF82, and (c) PBCF55. Each inset shows high-resolution TEM images revealing fringes.

Figure 2 shows the comparison of X-ray diffraction (XRD) patterns of the prepared layered double perovskite catalysts. The comparison of the overall XRD patterns (Figure 2a) of PBC, PBCF82, and PBCF55 reveal peaks that are well indexed to those characteristic of PrBaCo$_2$O$_{6-\delta}$ (P4/mmm) [JCPDS 00-053-0131] with minor amount of side oxide phases. The broad XRD peaks renders convolution of nearby peaks, and confirms the presence of nanoparticles as observed in TEM images. Apart from being in the same crystalline structure, the XRD peaks of PBCF82 and PBCF55 appear at a lower 2-theta value (Figure 2b) than PBC, which highlights that the perovskite structure exhibit larger lattice parameters upon the incorporation of Fe. The peaks of PBCF55 – the one with the highest Fe composition – appears at the lowest 2-theta value suggesting that PBCF55 would exhibit the largest lattice parameters among them. Considering the nature of ordered perovskites, which cations are
oriented in layers, the partial substitution of Co with Fe may lead to B-site cation octahedral tilting, which is difficult to separate from cation ordering.[8] Overall, the comparison of XRD patterns confirms that the layered double perovskite structure is withheld upon Fe incorporation while lattices may expand.

Figure 2. (a) Comparison of X-ray diffraction (XRD) patterns of PBC (black), PBCF82 (red), and PBCF55 (blue). The XRD patterns are well indexed to those of PrBaCo2O6-δ from literature [JCPDS 00-053-0131] (b) Magnified view of the main XRD peak.

2.2. Electrochemical Study

Systematic electrochemical characterizations are conducted in order to assess the functional role of Fe in activity and stability of the layered double perovskite catalysts during the OER process. Figure 3a shows constructed Tafel plots from measured steady-state currents from series of chronoamperometry studies of the prepared catalysts. In the presence of Fe, PBCF82 and PBCF55 revealed different Tafel slopes as compared to the non-doped PBC. PBCF82 and PBCF55 both showed similar Tafel slopes (~50 mV dec⁻¹) that are lower than that of the non-doped PBC (72 mV dec⁻¹) (Table 1). Our recent work investigated the functional role of Fe in the Co-based single randomly ordered perovskites, Ba:0.5Sr:0.5CoO₃₋δ and La:0.2Sr:0.8CoO₃₋δ, where remarkable enhancements in their OER activities were reported when doped with ~5 wt.% of Fe.[25] However, in this previous study, comparable Tafel slopes were observed for both non-doped and Fe-doped perovskites.[25] In contrast, here, the observed lower Tafel slope indicates that the catalyst would follow a different OER mechanism upon Fe incorporation, which may attribute to certain degree of changes of intrinsic physicochemical properties. PBCF82 and PBCF55 reveal higher current densities at 1.55 V_RHE (17.1 and 19.7 A g⁻¹, respectively) than compared to the non-doped PBC (13.8 A g⁻¹). Generally, lower Tafel slopes with increasing Fe composition in Co based catalysts have been observed by other studies.[32,34,43] All of the prepared layer perovskites revealed similar Brunauer-Emmett-Teller (BET) surface areas (Table S1), which shows that their differences in electrochemical activities are independent of their differences in surface area.
Figure 3. Electrochemical study comparing a) Tafel plot of OER activities and b) change in current densities with respect to the initial current density at every 25 cycles over 500 cycles between 1.0 and 1.6 V_{RHE} of PBC (black), PBCF82 (red), and PBCF55 (blue).

As previous studies\[2,44-46\] emphasize the importance of understanding the stabilities of electrode materials, the potential stability test was conducted during which currents are recorded as potential is stepped from 1.0 V_{RHE} to 1.6 V_{RHE} holding for 10 seconds at each potential for 500 cycles (see Figure 3b). Here the Fe-doping also showed a beneficial effect in functional stability such that PBCF55 reveals the least loss of current density over the period of cycles losing only about 32% of its initial current density, while PBC loses about 74%. PBCF82, which comprises less than half of Fe that is in PBCF55, demonstrates capability to retain about half of its initial current density at the end of the cycle (Table 1). In this comparison, the most enhanced activity and stability are demonstrated by a one-to-one Co:Fe ratio occupying the B-site of this particular double perovskite catalyst.

Table 1. Summary of electrochemical study results on OER activity and stability: apparent mass specific exchange current density \(j_0\), Tafel slope \(b\), activity expressed as mass specific current density at 1.54 V, and stability expressed as ratio of initial mass-specific current density and mass-specific current density after 500 cycles between 1.0 V_{RHE} and 1.6V_{RHE}.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>(j_0) (A g(^{-1}))</th>
<th>Tafel slope (mV dec(^{-1}))</th>
<th>(j @ 1.55 V_{RHE}) (A g(^{-1}))</th>
<th>(\Delta j) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBC</td>
<td>1.47</td>
<td>72</td>
<td>13.8</td>
<td>-73%</td>
</tr>
<tr>
<td>PBCF82</td>
<td>1.49</td>
<td>50</td>
<td>17.1</td>
<td>-52%</td>
</tr>
<tr>
<td>PBCF55</td>
<td>1.48</td>
<td>50</td>
<td>19.7</td>
<td>-32%</td>
</tr>
</tbody>
</table>

The functional stability of perovskite catalyst should be described based on the ability to sustain its initial electrocatalytic activity. In relation to the structural integrity, the catalyst should be capable to serve as a suitable substrate for the prospect of oxy(hydroxide) layer formation.\[25\] In this regard, Pourbaix diagrams are constructed based on density-functional theory (DFT) calculations to assess the thermodynamically stable phases of PBC and PBCF in aqueous solution (Figure S1a and b, respectively), from which phases of the catalyst under equilibrium conditions at OER potentials in a specified pH level are described. The Pourbaix diagrams of PBC and PBCF suggest the dissolution of A- and B-site cations. In fact, the cation dissolutions of perovskites are pointed out to be inevitable as governed by thermodynamics under the necessary OER conditions.\[44\] Nevertheless, it is necessary to highlight that the degradation mechanism is also driven by kinetics, which each perovskite catalyst would reach the end of its service life through different pathways based on the defect chemistry under the OER conditions.\[2,12,46\] In light of the above findings, the incorporation of Fe seems to
impede the rate of degradation, among which the one with the highest Fe composition (i.e. PBCF55) showed the most enhanced potential stability. Nonetheless, it should be noted that a higher composition of Fe (i.e. Fe-rich; x > 0.5) may compromise the role of Co as the active center and intrinsically undergo a different OER mechanism than Co-rich PBCF (i.e. x < 0.5) which would dim assessment of the functional role of Fe-doping.[34,43]

2.2. Operando X-ray Absorption Spectroscopy Study

The results of electrochemical studies revealed increasing OER activity and stability with increasing Fe composition in the domain of 0 ≤ x ≤ 0.5. As mentioned, PrBaCoO$_2$(1-x)Fe$_{2x}$Co$_{6-6x}$ with different Co to Fe composition ratios would follow different reaction pathways as they undergo different degradation processes under the OER condition. Therefore, operando X-ray absorption spectroscopy study is conducted in order to monitor the changes in local electronic and geometric structures of all the prepared layered double perovskites during the OER process, through which the functional effects of Fe are highlighted.

In Figure 4a, Co K-edge energy positions of normalized X-ray absorption near edge structure (XANES) spectra of as-prepared double perovskites reveal that PBC and PBCF’ve have Co oxidation state between +2 and +3, among which the Co K-edge position of PBCF55 is positioned at the lowest energy level. Through comparison, PrBaCoO$_2$(1-x)Fe$_{2x}$Co$_{6-6x}$ show reduced Co oxidation states with increasing Fe composition (i.e. x) in the following descending order: PBC > PBCF82 > PBCF55, each with ~0.3 eV difference in their Co K-edge energy position. Note, all edge energy positions were determined at the half the edge step. Figure 4b shows the comparison of the Fourier-transformed (FT) k$^2$-weighted Co K-edge extended X-ray absorption fine structure (EXAFS) spectra of as-prepared PBC, PBCF82, and PBCF55. The peaks of FT-EXAFS spectra signify the presence of neighboring atomic shells at specific radial distances from the absorbing atom (i.e. Co). In Figure 4b, the first two major peaks at ~1.9 Å and ~2.8 Å are ascribable to the backscattering contributions from the nearest Co–O and Co–Co/Fe ligands, respectively. Here, it is noteworthy that the second peak is ascribable to Co–Co coordination shell of the edge-sharing polyhedra typically found in highly oxygen deficient perovskite oxides prepared by flame spray synthesis (see Figure S2).[2,47,48] Inconveniently, this Co–Co/Fe ligand distance of edge-sharing polyhedra of PrBaCoO$_2$(1-x)Fe$_{2x}$Co$_{6-6x}$ is in close vicinity to that of Co/Fe-oxy(hydroxide) (refer to Supplementary Information S3 for detailed explanation). The next appearing peaks located at ~3.5 Å corresponds to Pr/Ba neighbors. All of the FT-EXAFS profiles of PBC, PBCF82, and PBCF55 show similar peak locations to one another suggesting that a similar local structure is maintained upon Fe incorporation. In Figure 4b, a decrease of the first peak amplitude is observed in the presence of Fe; listed in the descending order of amplitude: PBC > PBCF82 > PBCF55.

Given that the first peak is ascribable to Co–O coordination shell, Co of the layered double perovskite seems to be bound to less oxygen atoms at that radial distance in the presence of Fe. This is further verified by the best fit of the Co–O peak of FT-EXAFS spectra of as-prepared catalysts, which shows the decrease in Co–O coordination number with higher amount of Fe-doping (refer to Figure S8). Together with the comparison of XANES spectra, these findings lead to assert that more oxygen vacant sites are created with a higher amount of Fe-doping, and therefore reduces Co oxidation state in PrBaCoO$_2$(1-x)Fe$_{2x}$Co$_{6-6x}$. Moreover, the decrease of scattering intensities at farther radial distances observed in the FT-EXAFS spectra of both PBCF82 and PBCF55 is rationalized by octahedral distortions induced by doping of Fe (+3) into the B-site replacing Co (+2.7) cations which then weakens the backscattering from the neighboring atoms.[38,49-56]

Furthermore, Figure 4c and d display a comparisons of normalized XANES and FT-EXAFS spectra, respectively, of PBCF82 and PBCF55 recorded at the Fe K-edge. In Figure 4c, the edge energy positions of Fe K-edge XANES spectra of PBCF82 and PBCF55 indicates that their Fe oxidation states are similar (between +3 and +4). More precisely, the Fe K-edge of PBCF55 is positioned at about ~0.1 eV lower energy than PBCF82, but this insignificant difference would make the comparison trivial. Figure 4d shows Fe K-edge FT-EXAFS spectra of both PBCF82 and PBCF55 with similar scattering patterns as those of Co K-edge FT-EXAFS spectra. This confirms that Fe is indeed well integrated into the B-site of perovskite structure.
When a neutral oxygen vacancy is created, the left behind electrons would be distributed to either to Co and/or Fe, which would lower their oxidation states. However, the electrons are not evenly distributed among them but rather more accepted by Fe.[43,51] Based on above evidences, the addition of Fe seems to aid Co to be stable in a lower oxidation state by providing charge stabilization through balancing oxygen non-stoichiometry, and therefore promotes formation of oxygen vacancies. In the presence of higher oxygen vacancy concentration, the lattice oxygen within the perovskite structure is more inclined to participate in the water oxidation reaction (i.e. LOER) and develops the OER active oxy(hydroxide) layer at the surface.[3,30]

Figure 5a shows a shift of the Co K-edge XANES spectra to higher energy positions of PBC, PBCF82, and PBCF55 during the operando flow cell test, among which PBCF55 reveals the greatest extent of energy shift of ~0.7 eV at the highest potential, while PBC and PBCF82 display ~0.3 eV of edge shifts. Our previous studies showed that the positive Co K-edge shift during the OER process is attributed to the construction of the OER active oxy(hydroxide) layer; since the Co oxidation state of Co-oxy(hydroxide) layer is higher than those inherent in the perovskite oxide.[2,30] This also agrees with other DFT based studies.[49,50,54] Therefore, revisiting Figure 3a, the high OER activity of PBCF55 can be explained by the large extent of increase in the Co oxidation state, which is read from the shift of the Co K-edge position. At this point, we emphasize that the rate of dissolution (i.e. degradation) of a perovskite oxide catalyst during the OER process is controlled by its kinetics; thereby, each catalyst would reach its end-of-service life at a different rate. In this context, Figure 5b shows Co K-edge shifts at each increasing applied potential with respect to the energy positions collected at 1.2 V_RHE during the anodic polarization in flow cell test. In Figure 5b, Fe-doped PBCF82 and PBCF55 reveal rapid positive Co K-edge shifts when polarized into the oxygen evolution regime (> 1.4 V_RHE). The edge shift translates proportionally to the increase of Co oxidation state. This sudden increase of Co oxidation state when polarized above the OER onset signifies formation of the OER
active oxy(hydroxide) layer which is potential-induced. Meanwhile, in the absence of Fe, PBC shows a consistent increase even at potentials below the oxygen evolution regime indicating that the oxidation of its Co species are triggered by chemical dissolution.[2]

Particularly, even though the extent of shift of the Co K-edge position of PBCF82 is smaller than that of PBCF55, PBCF82 demonstrated a similar OER activity as PBCF55. Nevertheless, PBCF82 shows a rapid yet subtle increase of the Co oxidation state when polarized above the OER onset as similar to PBCF55 (Figure 5b). This may suggest the development of oxy(hydroxide) layer occurs but still less than in the case of PBCF55. Based on these observations, PBCF82 and PBCF55 both show different Co oxidation behaviors than compared to PBC suggesting that the catalyst would undergo a modified degradation pathway during the OER process upon Fe incorporation. Referring to the Tafel plot (Figure 3a), the difference in their Tafel slopes, where lower Tafel slopes are observed upon Fe-doping, may suggest that PBCFs would undergo different mechanism for OER than the non-doped PBC. Also referring to the stability test (Figure 3b), the inhibited degradation mechanism upon Fe incorporation is further supported by the improved current stabilities of PBCF82 and PBCF55. Although thermodynamics anticipate the dissolution of PrBaCo$_{2x}$Fe$_2$Co$_{6-x}$, it is intriguing to observe an enhanced ability to retain the initial current density upon Fe-doping, where PBCF55 demonstrated the highest retention of current density over the course of 500 cycles. The above findings point out that Fe plays an important role in improving the stability owing to the retardation of degradation mechanism. This does not mean that deterioration of the perovskite structure could be avoided but rather implies that the increase of Co oxidation state more due to the development of Co-ooxy(hydroxide) species. Hence, all of the catalysts under study show decreasing trend of current densities during the stability test. Therefore, the layered double perovskite can prolong as a substrate for the development of OER active oxy(hydroxide) species while the rate of chemical dissolution is lagged by the addition of Fe.

Despite of the clear indications as to which the construction of Co-ooxy(hydroxide) is displayed by positive edge shifts in their Co K-edge XANES spectra, this development – along with other concurrent local structural changes – are not clearly manifested in the comparison of FT-EXAFS spectra collected at potentials below and above the OER onset (1.2 and 1.54 V_{RHE}, respectively) (Figure S4a-c). Here, it is important to recapitulate the coinciding Co–Co radial distances between the edge-sharing polyhedra of PrBaCo$_{2x}$Fe$_2$Co$_{6-x}$ and the Co-ooxy(hydroxide) layer, both of which are at the proximity of ~2.8 Å from their primary Co atoms. In this respect, the FT-EXAFS profiles with these concurring signals would confound the precise interpretation of local structural changes. Considering these challenges, the first peak is fitted in order to verify the changes in the Co–O coordination during the OER process (summarized in Table S3 and Figure S8). The best fits show increased Co–O coordination numbers for all catalysts at the highest anodic potential (1.54 V_{RHE}) and therefore further consolidates the increase of Co oxidation states during the OER process.

While the increase of Co oxidation states are evident, Fe K-edge XANES spectra collected during the operando measurement (Figure 5c) reveal insignificant edge shifts (~0.1 eV) throughout the course of anodic polarization. Given that Fe in both PBCF82 and PBCF55 is, in relative terms, in a higher oxidation state (between +3 and +4) than Co (<+2.7) providing charge stability, the surplus electron upon to the removal of lattice oxygen in the path of LOER would go through Co as it has more empty states to accommodate extra charges;[51] this justifies the insignificant shift in the Fe K-edge. In this context, the formation of the active oxy(hydroxide) layer would therefore be accommodated more by Co polyhedra, and thereby less changes would be manifested in their Fe K-edge FT-EXAFS profiles (Figure S4).
Figure 5. (a) Comparison of Co K-edge XANES spectra of PBC, PBCF82, and PBCF55 recorded at 1.2 and 1.54 V$_{\text{RHE}}$ and (b) Co K-edge energy shift measured with respect to the edge position at 1.2 V$_{\text{RHE}}$ at each potential during operando flow cell tests. (c) Comparison of Fe K-edge XANES spectra of PBCF82 and PBCF55 recorded at 1.2 and 1.54 V$_{\text{RHE}}$. 
In light of our findings, the Fe incorporation into the layered double perovskite catalyst lead to stabilize Co in a lower oxidation state by providing a better charge distribution and promoting the formation of oxygen vacancies. Consequently, the degradation mechanism is inhibited such that the oxidation of Co is more induced by the increase of potential while its chemical dissolution is decelerated yet still unavoidable. The potential-induced Co oxidation behavior upon Fe-doping is indicative of the development of an OER active Co-oxo(hydroxide) surface layer. Despite of these enhancements, no significant electronic and structural changes were detected with respect to Fe. Overall, the addition of Fe seems to enable the layered double perovskite catalyst to improve its structural integrity (similar as previously observed for Ni,Fe1−xO2)[40] as a more suitable substrate for the construction of oxy(hydroxide) layer leading to enhanced OER activity and stability.

3. Materials and Methods

3.1 Material Synthesis

The flame spray synthesis setup is described by Heel et al.[57] For the preparation of the PrBaCoO5−y (PBC) and PrBaCo2−xFe2xO5−y (y = 0.4 and 1.0) precursor solutions, stoichiometric amounts of praseodymium oxide (Pr2O3, 99.9 %, Auer Remy), barium carbonate (BaCO3, ≥99%, Sigma-Aldrich), cobalt nitrate hexahydrate (Co(NO3)2·6H2O, 99.9%, Sigma-Aldrich) and iron nitrate nonahydrate (Fe(NO3)3·9H2O, ≥98%, Sigma-Aldrich) were dissolved in a mixture of solvents composed by N,N-Dimethylformamide (DMF, ≥99.8 %, Roth), acetic acid (HAc, ≥99.0%, Sigma-Aldrich), nitric acid (HNO3, 70%, Sigma-Aldrich) and water in 45:25:25 volume ratio, respectively. Firstly, the Pr2O3 was dissolved in the mixture of water and nitric acid at 80 °C; when a clear green solution was obtained, the BaCO3 was added and then, when no more CO2 bubbles were observed, the Co and Fe (only for PBCF solutions) metal precursors. When all dissolved, the HAc and the DMF were added, obtaining a final total metal concentration of 0.1 M. The precursor solutions were pumped into the flame by using a three piston pump (C-601, Büchi) with a flow controller (C-610, Büchi), using a constant flow free of pulsations of 20 mL/min. Pure oxygen (99.95%, Carbagas) was used as dispersion gas with a flow rate of 35 L/min. The combustion gas was formed by acetylene (99.6%, Carbagas), with a flow rate of 13 L/min, and pure oxygen (17 L/min). Finally, the powders were collected in a baghouse filter on four ashless paper filters (Whatman).

3.2 Material Characterizations

Phase characterization of prepared materials was performed using powder X-ray diffraction (XRD, Bruker D8 system in Bragg–Brentano geometry, Cu K-α radiation (λ = 0.15418 nm)). Specific surface area was calculated by Brunauer-Emmett-Teller (BET) analysis of N2 adsorption / desorption isotherms (AUROSORB-1, Quantachrome). Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) (TECNAI F30 operated at 300 kV) were used to study the surface morphology and composition of the prepared materials.

For ex situ and operando X-ray absorption spectroscopy (XAS) measurements, catalyst powders were dispersed in a mixture of isopropanol and Milli-Q water in the equal ratio sonicated for 30 min. The ink was then spray coated on Kapton film. XAS spectra at the Co K-edge and Fe K-edge were recorded at the SuperXAS beamline of the Swiss Light Source (PSI, Villigen, Switzerland). The incident photon beam provided by a 2.9 T superbend magnet source was collimated by a Si-coated mirror at 2.5 mRad (which also served to reject higher harmonics) and subsequently monochromatized by a Si (111) channel-cut monochromator. A Rh-coated toroidal mirror at 2.5 mRad was used to focus the X-ray beam to a spot size of 1 mm by 0.2 mm maximal on the sample position. The SuperXAS beamline[58] allowed for the rapid collection of 120 spectra during a measurement time of 60 sec (QEXAFS mode), which were then averaged. The spectra of samples were collected in transmission mode using N2 filled ionization chambers, where a Co foil (of Fe foil) was placed between the second and third ionization chamber as a reference to calibrate and align collected spectra. Extended X-ray absorption fine structure (EXAFS) spectra were analyzed using the Demeter...
software package,[59] which included background subtraction, energy calibration (based on the simultaneously measured Co reference foil) and edge step normalization. The resulting spectra were converted to the photoelectron wave vector k (in units Å⁻¹) by assigning the photoelectron energy origin, E₀, corresponding to k = 0, to the first inflection point of the absorption edge. The resulting χ(k) functions were weighted with k² to compensate for the dampening of the EXAFS amplitude. These χ(k) functions were Fourier transformed over 3 – 12 Å⁻¹ and plotted. The scattering paths used for the EXAFS fittings of all catalysts were generated from the structure of CoOOH[60] for the first Co–O coordination shell using the FEFF6.2 library. Refer to Supplementary Information S4 for detailed description of EXAFS fittings.

3.3 Electrochemical Characterization

The electrochemical activities of the prepared catalysts were evaluated in a standard three-electrode electrochemical cell with the thin-film rotating disk electrode (RDE).[61] The setup for OER and cyclic voltammetry (CV) consists of a potentiostat (Biologic VMP-300) and a rotation speed controlled motor (Pine Instrument Co., AFMSRCE). All the electrochemical measurements were performed at standard room temperature using a reversible hydrogen electrode (RHE) as the reference electrode in 0.1 M KOH. A gold mesh was used as the counter electrode. A Teflon cell was used to contain the electrolyte with the electrodes immersed under potential control. A porous thin film electrode was prepared by drop-casting a catalyst ink on a polished glassy carbon electrode (5 mm OD / 0.196 cm²).[61] The catalyst ink was prepared from a catalyst suspension made from sonicating (Bandelin, RM 16 UH, 300 Weff, 4 mm OD / 0.196 cm²). The resulting spectra were converted to the photoelectron wave vector k (in units Å⁻¹) by assigning the photoelectron energy origin, E₀, corresponding to k = 0, to the first inflection point of the absorption edge. The resulting χ(k) functions were weighted with k² to compensate for the dampening of the EXAFS amplitude. These χ(k) functions were Fourier transformed over 3 – 12 Å⁻¹ and plotted. The scattering paths used for the EXAFS fittings of all catalysts were generated from the structure of CoOOH[60] for the first Co–O coordination shell using the FEFF6.2 library. Refer to Supplementary Information S4 for detailed description of EXAFS fittings.

First, 25 reverse potentiostatic sweeps of CV were conducted in synthetic air-saturated electrolyte from 1.0 to 1.7 V_RHE at a scan rate of 10 mV s⁻¹. Then, chronoamperometric measurements were carried out holding each potential step for 30 seconds to obtain steady-state currents at each potential from 1.2 to 1.7 V_RHE while rotating the working electrode at 900 rpm. The potential stability of catalyst materials was conducted using the same setup; by stepping potential between 1.0 and 1.6 V_RHE 500 times holding 10 seconds at each potential to collect currents at steady-state. Five cycles of CV and electrochemical impedance spectroscopy (EIS) were carried out after every 100 cycles. All measured currents were normalized by the mass of catalyst loading, and potentials were corrected for the ohmic drop obtained from EIS.

3.4 Operando Flow Cell Study

The homemade operando XAS electrochemical flow cell used in this study was extensively described previously.[62] As explained in section 3.2, electrode materials were spray coated at the center of Kapton films. Black pearl-2000 (Cabot Corp.) was used as the counter electrode material. A silver chloride electrode (Ag+/AgCl) (Hugo Sachs Elektronik) was used as the reference electrode. During electrochemical testing, the electrolyte was drawn into the cell and collected in a syringe at the flow rate of 0.1 mL min⁻¹. The chronoamperometry measurement was carried out holding for 120 sec at each anodic potential step from 1.2 V_RHE to 1.54 V_RHE, and again during the reverse sequence back to 1.2 V_RHE. At each potential step, both transmission XAS spectra at the Co and Fe K-edges were collected simultaneously for 60 seconds. The energy position of Co and Fe K-edge were read with respect to the half of the edge-step.

3.5 Density-Functional Theory – Pourbaix Diagrams

Density-functional theory (DFT) calculations are used to help understand the experimental data. In the first set of calculations, the stability of the perovskites in an aqueous environment was investigated by means of Pourbaix diagrams. This method has been previously used to investigate
the stability of Ru-based perovskites in water as a descriptor for the stability in water to identify novel light harvesting materials.[63] Pourbaix diagrams show the phase diagram of solid and dissolved species as a function of pH and applied potential (V_{\text{SHE}}). DFT provides the total energies for the solid bulk for the perovskites and the other solid competing phases as described in the Materials Project database.[64] Experiments provide the dissolution energies for the dissolved species.[65,66] This method is implemented in the Atomic Simulation Environment (ASE) package,[67] and more details about the methodology can be found in the literature.[68,69] All the bulk structures have been fully relaxed using the Quantum ESPRESSO code,[70] PBEsol as exchange-correlation functional,[71] and the pseudopotentials from the Standard Solid State Pseudopotential library (SSSP accuracy).[72]

4. Conclusion

In here, a systematic study is conducted to assess the role of Fe in the highly OER active layered double perovskite catalyst, PrBaCo_{2+\delta}Fe_{2-\delta}O_{6-\delta}, by comparing different compositions of Fe: PBC (x = 0), PBCF82 (x = 0.2), and PBCF55 (x = 0.5). These layered double perovskite catalysts are prepared via flame spray synthesis, where Fe is indeed incorporated into the B-site as verified by XRD and FT-EXAFS profiles. In comparison to PBC, Fe-doped PBCF82 and PBCF55 revealed enhanced OER activities and improved current stabilities as to better retain the initial current density. At the basis of our findings, such enhanced electrocatalytic performance is attributed to the addition of Fe, which provides charge stability as to compensate for the oxygen non-stoichiometry, which allows Co to be in a lower oxidation state. This leads to alteration of the oxidation behavior of the layered double perovskite catalyst upon anodic polarization so that its Co oxidation is predominantly provoked by the increase of applied potential. The charge stability is established upon the addition of Fe, which favors to accept the surplus charges left behind by the formation of oxygen vacancy. In addition, the potential-induced Co oxidation upon Fe-doping is attributed to the formation of OER active oxy(hydroxide) layer at the surface. This also implies that the perovskite structure is prolonged under the OER conditions so that it serves as a substrate for the construction of oxy(hydroxide) layer at the surface. It should be noted that even in the presence of Fe the catalyst is not exempted from the inevitable cation dissolution under the OER conditions as governed by its thermodynamic nature. All of these effects lead to highlight the constructive role of Fe in the layered double perovskite as OER catalyst, which are evident in lower Tafel slopes and enhanced current density stabilities of PBCF82 and PBCF55. Particularly, PBCF55 – with the highest Fe composition – demonstrated great enhancements in both activity and stability as OER catalyst.

In summary, these results lead to conclude that layered double perovskite catalyst is intrinsically modified upon Fe-doping to become more resilient to the cation dissolution, and thereby prolong as substrate for the development of an oxy(hydroxide) surface layer. This leads to attain a higher activity towards oxygen evolution reaction. As conventionally seen from many transition metal oxide catalysts, such electrocatalytic performance enhancements are attributed to the synergy between Fe and Co. In this regard, it should be emphasized that the incorporation of Fe would modify the degradation mechanism of the host transition metal. Thus, it should be generalized that the electrocatalytic performance of a doped-metal oxide would rely on the interaction between the host transition metal and the dopant metal. These findings present a systematic study method to engineer and design an ideal perovskite oxide as OER catalyst.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: Density-functional theory calculated Pourbaix diagrams, Figure S2: Illustration of Co–Co distance, Figure S3: Comparisons of Co K-edge FT-EXAFS profiles with that of γ-CoO(OH), Figure S4: Comparison of FT Co K-edge EXAFS spectra collected during the operando XAS measurements, Figure S5: Best fitted Co K-edge FT-EXAFS spectra of PBC, Figure S6: Best fitted Co K-edge FT-EXAFS spectra of PBCF82, Figure S7: Best fitted Co K-edge FT-EXAFS spectra of PBCF55, Figure S8: Comparison of coordination number (N_{\text{Co-O}}) of the first peak of FT-EXAFS spectra, Table S1: Summary of BET surface areas of the prepared catalysts, Table S2: PrBaCo_{2(1-x)}Fe_{2x}O_{6-\delta} calculated from Rietveld refinement of X-ray diffractions, Table S3: Summary of best fit parameters of Co K-edge FT-EXAFS spectra.
Author Contributions: conceived, conceptualized, B.K., E.F., and T.J.S.; synthesis, M.B. and T.G.; characterizations, electrochemical measurements, investigation, B.K.; DFT computations, I.E.C.; all authors discussed the results and commented on the manuscript.

Funding: This research was funded by Swiss National Science Foundation, Innosuisse and the Swiss Competence Center for Energy Research (SCCER) Heat and Paul Scherrer Institute

Acknowledgments: The authors gratefully acknowledge the Swiss National Science Foundation through its Ambizione Program and the NCCR Marvel, the Swiss Competence Center for Energy Research (SCCER) Heat & Electricity Storage through Innosuisse, Switzerland, and Paul Scherrer Institute for financial contributions to this work, respectively. The authors thank the Swiss Light Source for providing beamtime at the SuperXAS beamline.

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


for oxygen evolution reaction: Insights into activity and stability of ba0.5sr0.5co0.8fe0.2o2+delta and prbaco2o5+delta. Adv. Funct. Mater. 2018, 28.


51. Mueller, D.N.; De Souza, R.A.; Brendt, J.; Samuelis, D.; Martin, M. Oxidation states of the transition metal cations in the highly nonstoichiometric perovskite-type oxide ba0.1sr0.9co0.8fe0.2o3-delta. *J. Mater. Chem.* 2009, 19, 1960-1963.


57. Heel, A.; Holtappels, P.; Hug, P.; Graule, T. Flame spray synthesis of nanoscale lα0.65sr0.4co0.2fe0.8o3-delta and ba0.5sr0.5co0.8fe0.2o3-delta as cathode materials for intermediate temperature solid oxide fuel cells. *Fuel Cells* 2010, 10, 419-432.


64. The materials project. [https://materialsproject.org/](https://materialsproject.org/) (Nov. 2017).


Standard solid state pseudopotential library. [http://materialscloud.org/sssp](http://materialscloud.org/sssp)