Supplementary Material for

Synthesis of bifunctional BaFe_{1-x}Co_xO_{3-y- δ}(OH)_y catalysts for the oxygen reduction reaction and oxygen evolution reaction

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X	A Site	B Site	Fe	Со
0	1	1	0	1
0.1	0.91	1.09	0.12	0.88
0.2	0.91	1.09	0.19	0.81
0.3	0.91	1.09	0.29	0.71
0.4	0.94	1.06	0.40	.60
0.5	1	1	0.49	0.51
0.6	0.91	1.1	0.61	0.39
0.7	0.92	1.08	0.70	0.30
0.8	0.89	1.1	0.85	0.15
0.9	0.95	0.11	0.89	0.11
1	0.90	1.1	1	0

Table S1:- EDX results for the series BaFe1-xCoxO3-y- δ (OH)y. Table S1a shows the A to B site ratio and Table S1b shows the Fe to Co ratio.

A study of the high temperature structural and water loss behavior of BaFe_{0.5}Co_{0.5}O_{3-y-δ}(OH)_y

The temperature dependence of the stabilization is very important for materials to become potential candidates for PCFC electrode catalysts, and we studied this behavior exemplarily by a combination of methods for the compound with x = 0.5.

The water loss behaviour and determination of the amount of crystal water could be studied using STA. Figure S 1a shows the STA measurement of the sample with x = 0.5. TGA data accompanied with the endothermic signal indicated the initial steep weight loss between 400 K and 550 K. This weight loss can be further followed from the elemental hydrogen analysis (Figure S 1b) carried out on the powder of the same composition heated to different temperatures. Between 400 K and 550 K there is approximately 40 % loss of the crystal water. Above 550 K, the weight loss continues at a lower rate until 800 K, at which a clear kink in the TGA curve is observed. A total mass loss of ~ 2.8 – 3.0 % was found, which corresponding to 0.37 - 0.40 H₂O per formula unit of BaFe_{0.5}Co_{0.5}O_{3-x}, which is in well agreement with the 0.37(2) H₂O per formula unit as obtained from elemental hydrogen analysis. In combination with the result from the iodometric titration,

the composition of the sample after synthesis can therefore be approximated to be $BaCo_{0.5}Fe_{0.5}O_{2.44}(H_2O)_{0.37} = BaCo_{0.5}Fe_{0.5}O_{2.81}H_{0.74} = BaCo_{0.5}Fe_{0.5}O_{2.07}(OH)_{0.74}$. The amount of crystalline water is lower than found for the compounds with x = 0 and 1.

Ex-situ FT-IR measurements were also carried out for BaCo_{0.5}Fe_{0.5}O_{2.07}(OH)_{0.74} powder heated to various temperature upto 773 K (Figure S 1c) to confirm the presence of the protons. The presence of protons could be confirmed up to temperature of 623 K, after which the broad band around 3300-3500 cm⁻¹ (corresponding to the OH stretching band ^{1,2}) could not be observed further. Again, this is in agreement with the TGA studies as well as the elemental hydrogen analysis performed on the compound (taking into account that longer prevalence times at higher temperatures were used for the samples studied with FT-IR, whereas the TGA is a more dynamic method).



Figure S 1: (a) TGA/DSC and (b) elemental hydrogen analysis on $BaCo_{0.5}Fe_{0.5}O_{2.07}(OH)_{0.74}$ under a flow of argon. (c) FT-IR spectra recorded for $BaFe_{0.5}Co_{0.5}O_{2.05}(OH)_{0.78}$ up to 773 K. The presence of protons could be confirmed till 623 K.

To study the structural changes upon water loss, high temperature X-ray diffraction (Figure S 2a) was carried out. Consistent with the STA and elemental hydrogen analysis studies, HT-XRD shows significant changes in the diffraction pattern between 373 K and 473 K which is attributed to loss of crystal water. At 473 K, the recorded diffraction pattern

shows similarity with that of BaFeO_{2.5}³, which could be confirmed by Rietveld analysis (Figure S 2b, monoclinic space group $P2_1/c$, a = 6.975(4) Å, b = 11.728(6) Å, c = 23.450(5)Å, β = 98.813(5) ° and Z= 28). This monoclinic setting is maintained till 773 K and also further down upon cooling to room temperatures. Similar behaviour was observed for BaFeO_{2 333}(OH)_{0 333}², for which BaFeO_{2 5} is the water free analog. Water loss can also be followed from the decrease in unit cell volume, represented by plotting pseudocubic lattice parameter with the temperature as shown in Figure S 2c. The decrease in the pseudocubic lattice parameter around 473 K is consistent with the water loss and in agreement with the STA and elemental hydrogen analysis. An increased unit cell volume of the hydrated phases is also consistent with the previous reports on similar perovskite oxide compounds which can incorporate large amount of water inside the crystal lattice.eg BalnO_{2.5} to BalnO₂(OH)⁴ and BaFeO_{2.5} to BaFeO_{2.33}(OH)_{0.33}². Further heating to 773 K causes an increase in the pseudocubic lattice parameters due to thermal expansion. On cooling down, a small difference to the cell volume on heating could be observed, which agrees well with the prevalence of water within the compound during heating. This loss is completed at higher temperatures (773 K), well agreeing with this behavior.



Figure S 2: (a) High temperature X-ray diffraction patterns for BaCo_{0.5}Fe_{0.5}O_{2.07}(OH)_{0.74} measured under a flow of argon till 773 K. (b) Rietveld fit for the X-ray diffraction pattern recorded at 473 K under flow of argon.

(c) Pseudocubic lattice parameters obtained from the refinement of HT-XRD data of $BaCo_{0.5}Fe_{0.5}O_{2.08}(OH)_{0.74}$.

X	Oxygen Content	Water Content per	Unit Formula
	per formula unit	formula unit	
0	2.50	0.452	BaFeO _{2.05} (OH) _{0.90}
0.1	2.50	0.409	BaFe _{0.9} Co _{0.1} O _{2.09} (OH) _{0.82}
0.2	2.48	0.39	BaFe _{0.8} Co _{0.2} O _{2.09} (OH) _{0.78}
0.3	2.46	0.382	BaFe _{0.7} Co _{0.3} O _{2.08} (OH) _{0.76}
0.4	2.45	0.372	BaFe _{0.6} Co _{0.4} O _{2.08} (OH) _{0.74}
0.5	2.44	0.37	BaFe _{0.5} Co _{0.5} O _{2.07} (OH) _{0.74}
0.6	2.37	0.373	BaFe _{0.4} Co _{0.6} O _{2.00} (OH) _{0.74}
0.7	2.35	0.380	BaFe _{0.3} Co _{0.7} O _{1.97} (OH) _{0.76}
0.8	2.32	0.394	BaFe _{0.2} Co _{0.8} O _{1.93} (OH) _{0.78}
0.9	2.27	0.413	BaFe _{0.1} Co _{0.9} O _{1.86} (OH) _{0.82}
1	2.23	0.432	BaCoO _{1.80} (OH) _{0.86}

Table S 2:- Tabulation of X dependence on oxygen, water content and composition per formula unit.

site	δ [mm s−1]	ε [mm s−1]	BHF [T]	
Fit D1	0.383(28)	1.317(48)		Fitted
Fit Sext1	0.074(31)	0*	20.50(21)	inside
Fe5, CN = 5	0.37(1)	-0.50(2)	49.2(5)	
Fe6, CN = 5	0.33(1)	-0.64(2)	47.3(5)	
Fe2-4,b CN = 4	0.15(1)	-0.2c	40.0(5)	

Table S 3: Mössbauer parameters of BaCo0.5Fe0.5O2.07(OH)0.74 at room temperature



Figure S 3. Tafel analysis of series $BaFe_{1-x}Co_xO_{3-y-\delta}(OH)_y$ (x = 0, 0.2, 0.5, 0.8, 1) for both the (a) ORR and (b) OER. Tafel plots were obtained for the measurements of the catalysts plus carbon additive.



Figure S 4: a) & b) Binding energies of Co3p peaks as a function of X. c) XPS spectra of the valence band for the series $BaFe_{1-x}Co_xO_{3-y-\delta}(OH)$ (x = 0, 0.2, 0.5, 0.8, 1).



Figure S 5: Bifunctionality parameter for x= 0, 0.2, 0.5, 0.8, 1 of the series $BaFe_{1-x}Co_xO_{3-y-\delta}(OH)_y$ recorded for U_{OER} at 10 mAcm/cm⁻² and U_{ORR} at 2.5mA/cm⁻²

	ORR			OER	
Catalysts	U _{onset} (V vs RHE)	E1/2 (V vs RHE)	Tafel slope (mV/dec)	U _{onset} * (V vs RHE)	Tafel slope (mV/dec)
X=1	0.788	0.662	102	1.63	162
X=0.8	0.780	0.672	91	1.57	172
X=0.5	0.780	0.660	66	1.57	70
X=0.2	0.798	0.675	84	1.55	190
X=0	0.803	0.251	125	1.58	149

* The Uonset of OER were defined as the intercept of the curve on the x-axis

Table S 4: Tabulated data of electrocatalytic activities for the perovskite-based $BaFe_{1-x}Co_xO_{3-y-\delta}(OH)_y$ catalysts.



Figure S 6. (a) ORR and OER activity data obtained in 0.1M KOH for the samples of the series $BaFe_{1-x}Co_xO_{3-y-\delta}(OH)_y$ (x = 0, 0.2, 0.5, 0.8, 1) as measured <u>without</u> carbon additive. (b) Kinetic current density as a function of Fe fraction for ORR of the series $BaFe_{1-x}CoxO_{3-y-\delta}(OH)$ with and without carbon additive. (c) Over potentials for different current densities as a function of Fe fraction for OER of the series $BaFe_{1-x}CoxO_{3-y-\delta}(OH)$. All shown data were e corrected for the ohmic electrolyte resistance (iR). Error bars represent standard deviations from two to three independent measurements.

2 References

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