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## Effect of Ball Milling on Electrocatalytic Activity of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ toward Oxygen Evolution Reaction

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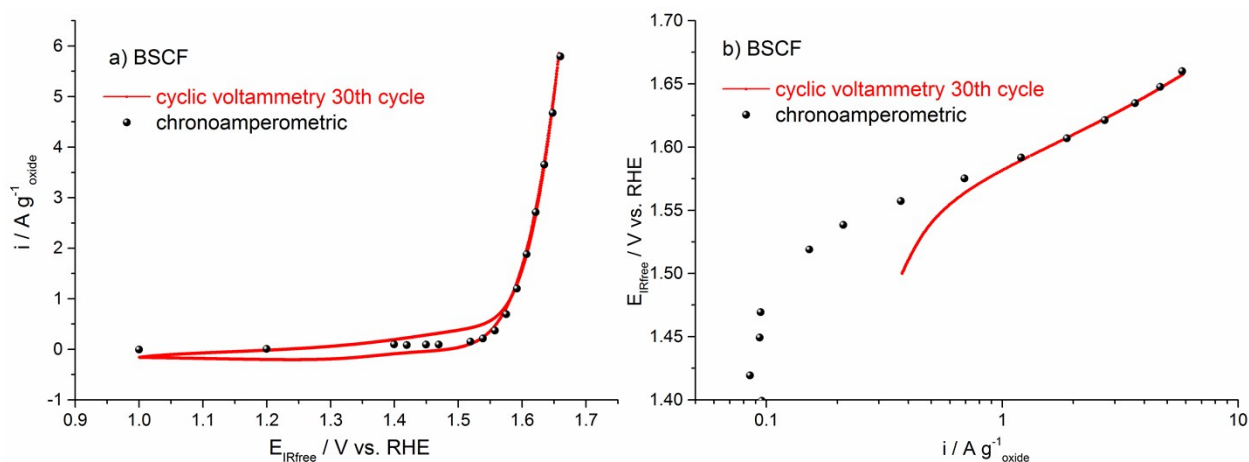
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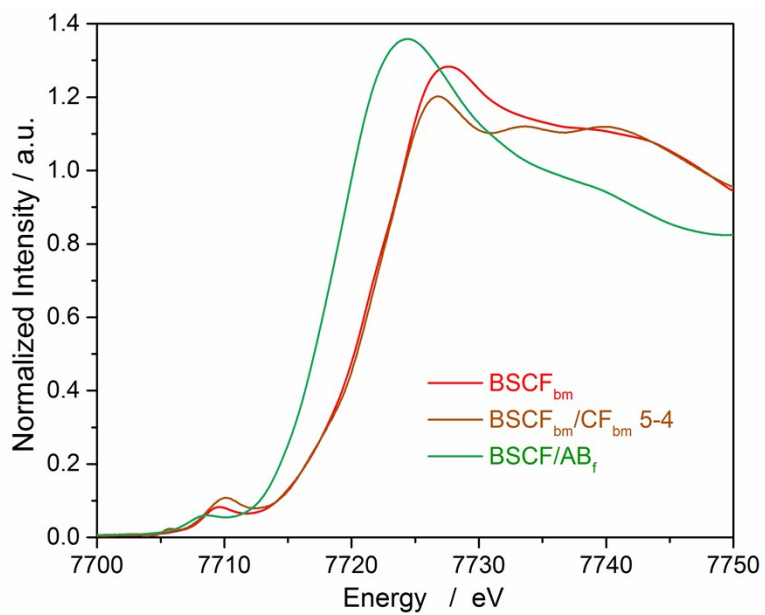
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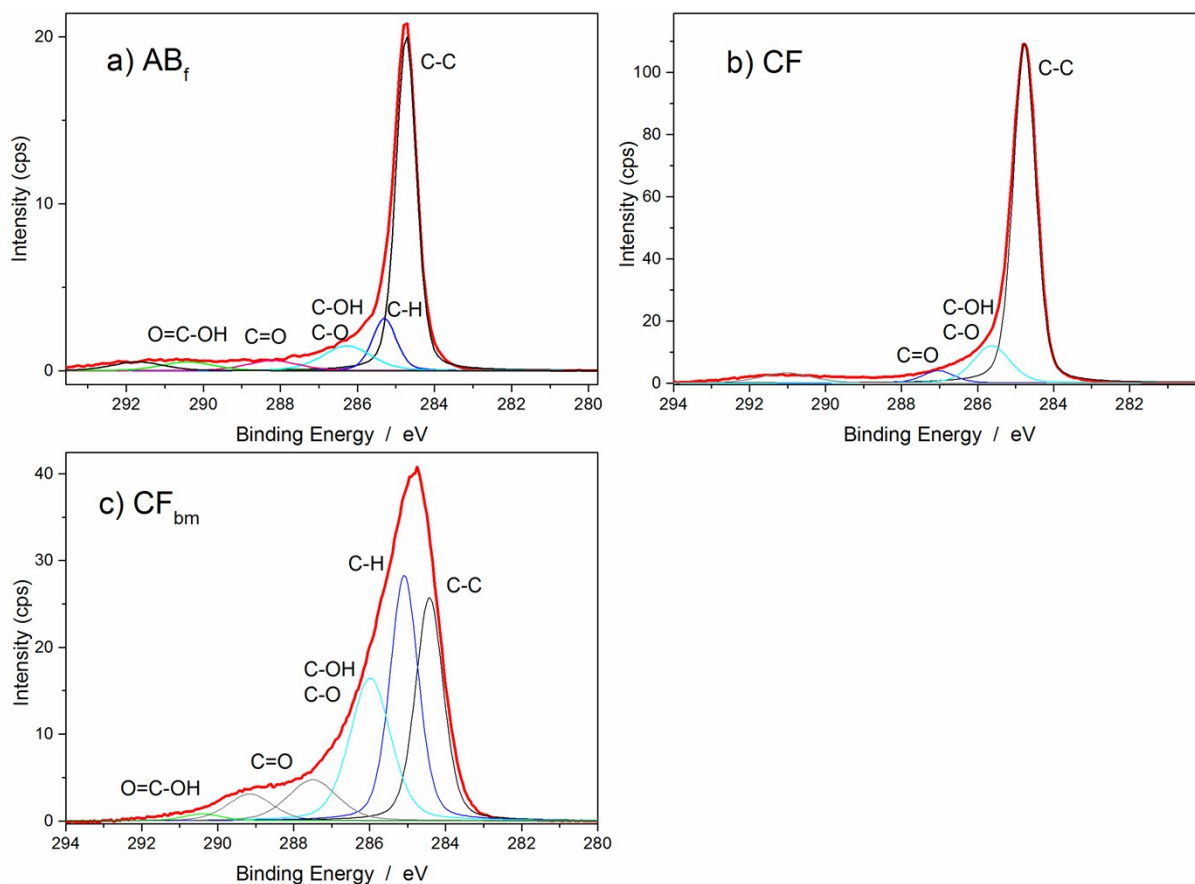
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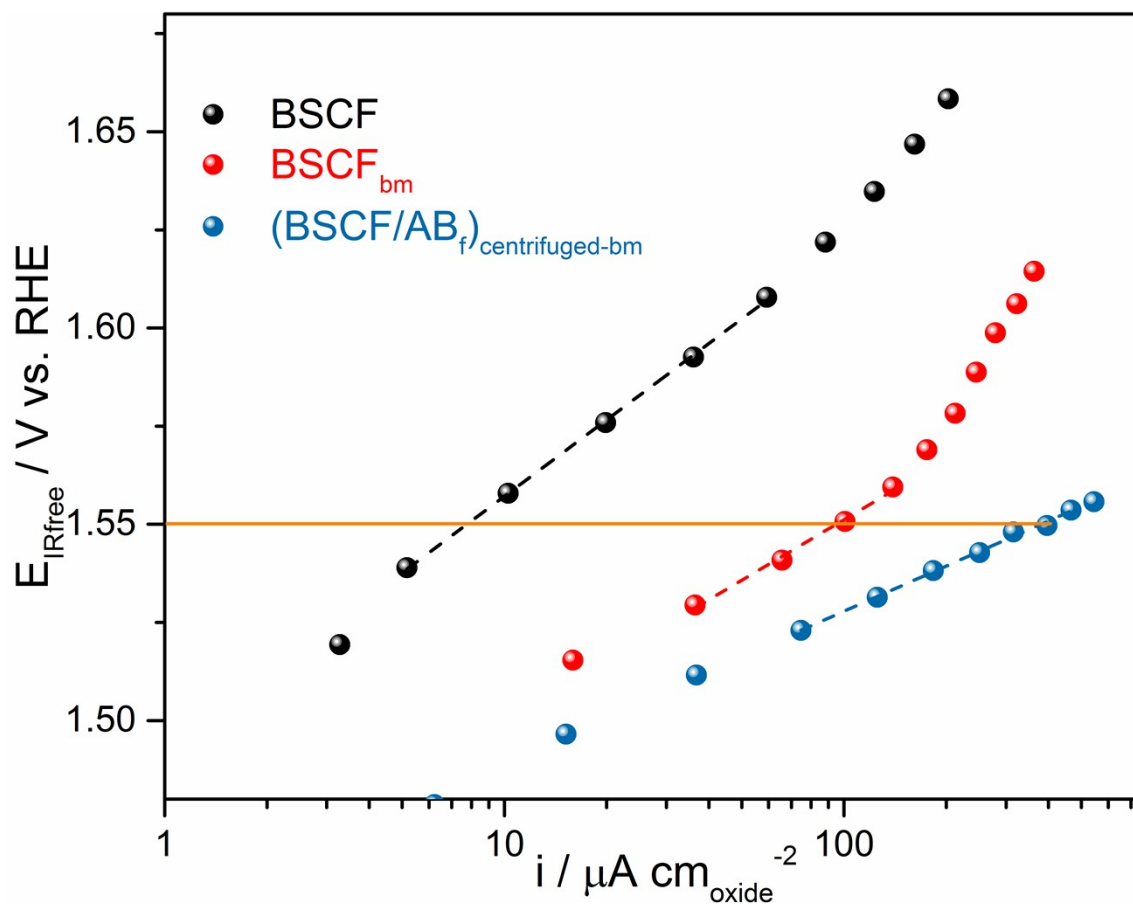
**Figure S1.** a) Comparison between cyclic voltammetry ( $10 \text{ mV s}^{-1}$ ) versus chronoamperometry (holding each potential for 30 s) measurements for BSCF electrode in synthetic air-saturated 0.1 M KOH at 1600 rpm. The chronoamperometry measurement allows obtaining an almost steady-state current with no capacitive contribution. b) Tafel curves of BSCF electrode obtained by a cyclic voltammetry measurement at  $10 \text{ mVs}^{-1}$  and by a chronoamperometry experiment by holding each potential for 30 sec in synthetic air-saturated 0.1 M KOH at 1600 rpm.



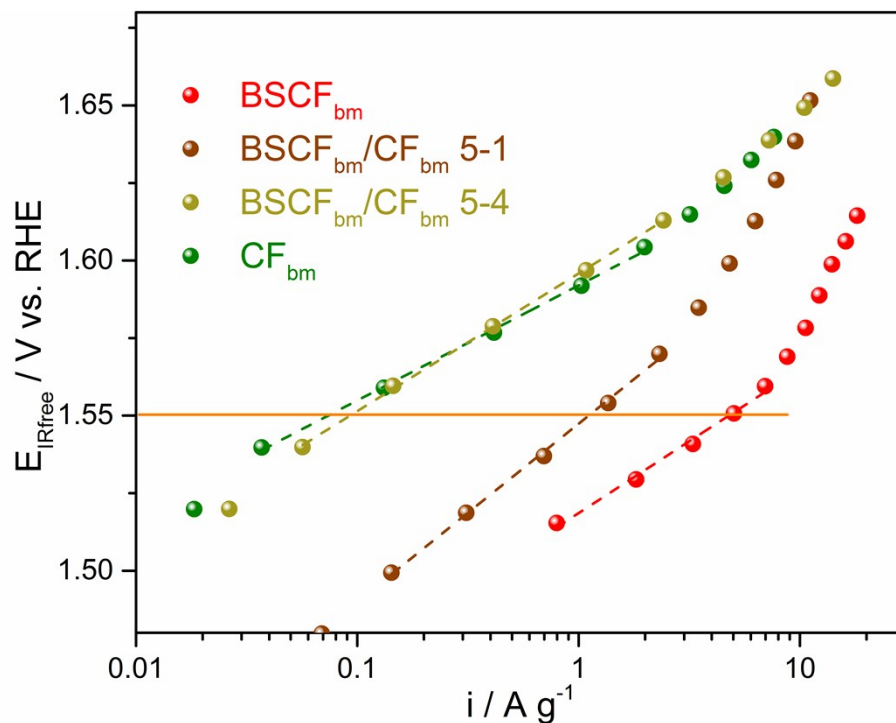
**Fig. S2.** XANES spectra at Co K edges for BSCF<sub>bm</sub>, BSCF<sub>bm</sub>/CF<sub>bm</sub> 5-4 and BSCF/AB<sub>f</sub> at room temperature.



**Fig. S3.** X-ray photoelectron spectroscopy (XPS) C 1s of a) functionalized Acetylene black (AB<sub>f</sub>), b) Carbon fiber (CF) and c) Carbon fiber ball milled (CF<sub>bm</sub>) in a stainless steel vial at 300 rpm under air atmosphere using the Fritsch Pulverisette 7 ball mill. The ball milling is switched on and off at intervals of 10 minutes to avoid overheating, the total ball milling process is 24 hours.



**Fig. S4.** OER Tafel slope obtained by chronoamperometry measurements for BSCF, BSCF<sub>bm</sub> and (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> electrode. The current is normalized by the BET surface area of oxide.

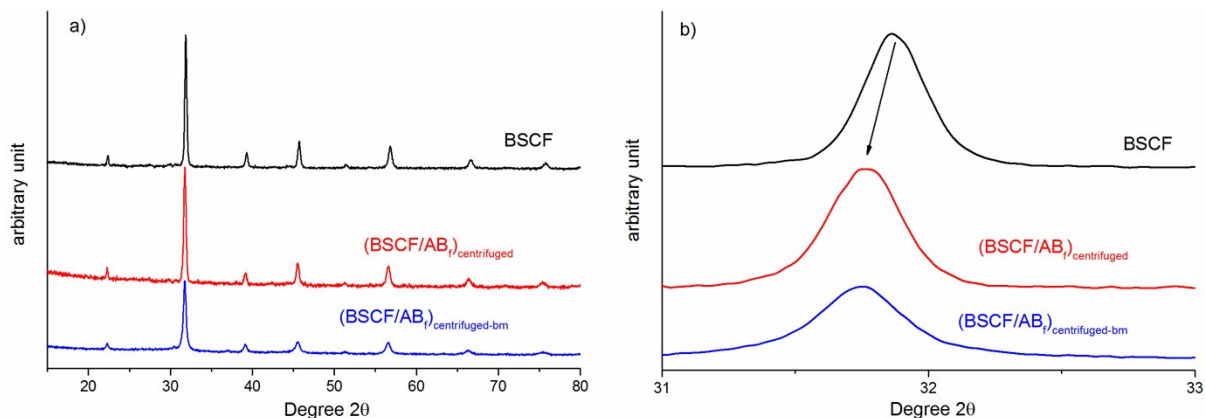


**Fig. S5.** OER Tafel slope obtained by chronoamperometry measurements for BSCF<sub>bm</sub>, BSCF<sub>bm</sub>/CF<sub>bm</sub> in ratio 5:1 by weight, BSCF<sub>bm</sub>/CF<sub>bm</sub> in ratio 5:4 by weight and CF<sub>bm</sub> electrode. As discussed in the manuscript, BSCF and CF ball milled separately and followed by joint ultrasonication in isopropanol cannot reduce the Co oxidation state (**Figure S2**). Thus, when there is no direct BSCF-carbon interaction, the presence of CF<sub>bm</sub> has a pure inhibition effect on the OER activity of BSCF<sub>bm</sub>.

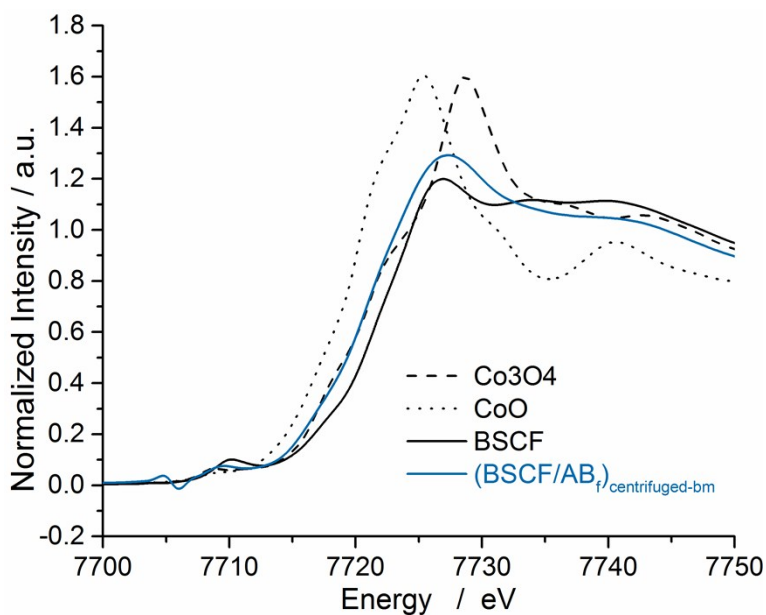
### **Preparation and Characterization of $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged}}$ and $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged-bm}}$ .**

BSCF was functionalized mixing BSCF and  $\text{AB}_f$  in a 5:1 ratio in isopropanol and then ultrasonically suspending the suspension for 30 min. The  $\text{BSCF}/\text{AB}_f$  suspension was centrifuged at 1000 rpm for 1 min, which allows precipitating the BSCF component but not the  $\text{AB}_f$ . Successively the suspended  $\text{AB}_f$  in isopropanol was removed and finally fresh isopropanol was added. The same procedure was repeated several times until no carbon in suspension was observed. The  $\text{AB}_f$  free  $\text{BSCF}/\text{AB}_f$  powder was then dried in air at 60°C and noted as  $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged}}$ . The substantial removal of the carbon component from the  $\text{BSCF}/\text{AB}_f$  composite was confirmed by XRD analysis which did not show any signal related to an amorphous carbon phase in the XRD pattern of the  $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged}}$  powder (figure 5Sa). Figure 5Sb shows a clear shift of the  $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged}}$  (110) diffraction peak towards lower angles compared to that of BSCF, corresponding to an increase of the lattice parameter from 3.97 to 4.01 Å, respectively. This increase can be ascribed to the reduction of the Co oxidation state in  $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged}}$  compared to that of BSCF, as revealed by our previous XANES reports.<sup>1, 2</sup> The  $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged}}$  powder was then ball milled in a stainless steel vial at 300 rpm under air atmosphere using a Fritsch Pulverisette 7 ball mill. The ball milling is switched on and off at intervals of 10 minutes to avoid overheating, the total ball milling process is 24 hours. The ball milled sample is noted as  $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged-bm}}$ . Figure 5Sa shows that the ball milling procedure does not destroy the composition of BSCF. Nevertheless, the broadened diffraction peaks displayed by  $(\text{BSCF}/\text{AB}_f)_{\text{centrifuged-bm}}$  powders indicate decreased crystallite sizes after ball milling. Figure 5Sb shows that the

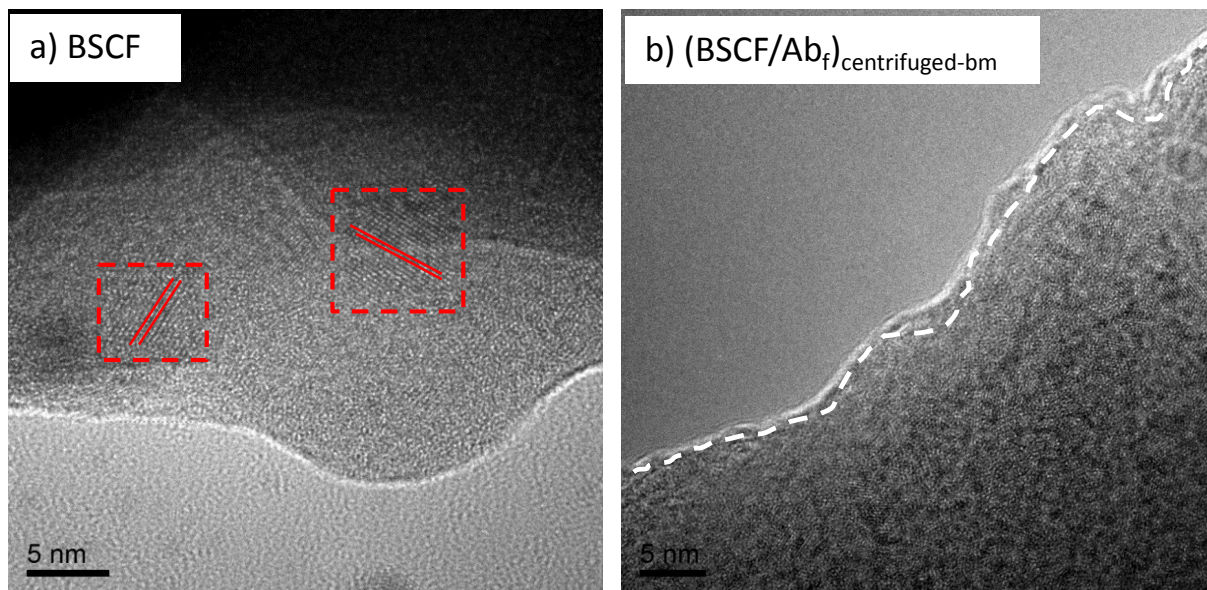
(BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> (110) diffraction peak retains the shift towards lower angles compared to that of BSCF. Figure S6 confirms the retaining of the reduction of the Co oxidation state in in (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> compared to that of BSCF.



**Fig. S6.** a) XRD patterns for the BSCF, (BSCF/AB<sub>f</sub>)<sub>centrifuged</sub> and (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> powders; b) (110) diffraction peak for the BSCF, (BSCF/AB<sub>f</sub>)<sub>centrifuged</sub> and (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> powders.

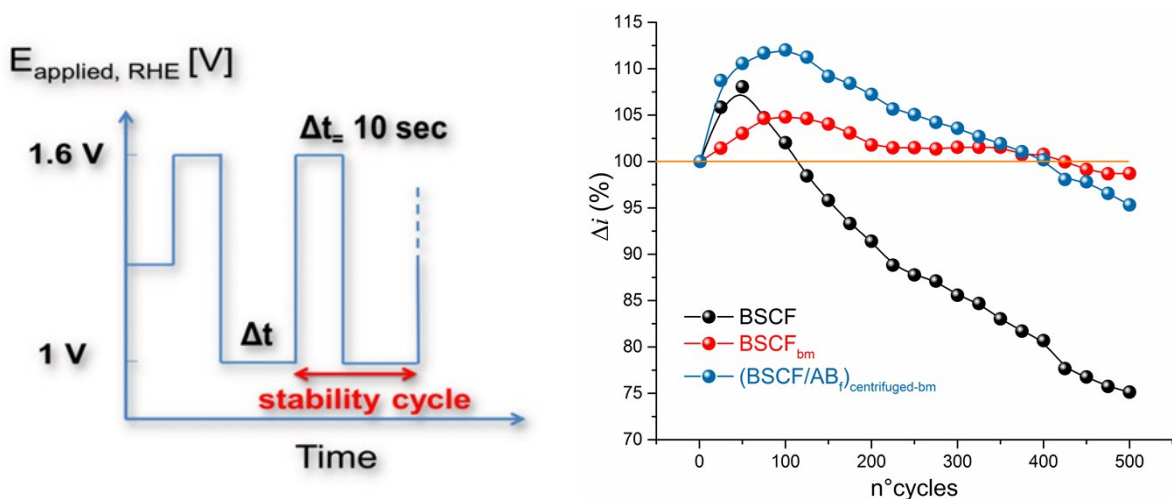


**Fig. S7.** XANES spectra at the Co K-edge for BSCF and (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> powders.



**Fig. S8.** High-resolution transmission electron microscopy (HRTEM) of (a) BSCF powders and (b) (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> powders. The red line serves a guide for the eyes for the atom column in crystalline BSCF sample, while the white line identifies the amorphous region in the (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> sample.





**Fig. S9.** Initially, 25 cyclic voltammograms were performed in the synthetic air-saturated 0.1 M KOH between 1.0 and 1.7 V RHE at a scan rate of  $10 \text{ mV s}^{-1}$ . Then chronoamperometric measurements were carried out to measure the OER activity holding each potential step for 60 seconds in the same range of potentials as in CV while rotating the working electrode at 1600 rpm. Subsequently, the stability protocol consists of switching the potential between 1 and 1.6 V RHE in 0.1 M KOH electrolyte, with a holding time at each potential for 10 sec and a rotation rate of 1600 rpm to avoid bubble formation. Each potential switch between 1 and 1.6 V RHE has been repeated 500 times (number of cycles). Every 25 cycles the chronoamperometric measurement between 1.0 and 1.7 V RHE has been recorded and the electrode activity is evaluated at 1.6 V RHE. To better compare the stability of the three samples which have a very different current density, here we show the delta current in percentage instead of the current density normalized by oxide mass. For all samples, the current measured increases with the number of cycles in the first 50-100 cycles. Then the current decreases with increasing cycles. After 500 cycles, the current density of BSCF electrode reduces by 25% while the decrease for BSCF<sub>bm</sub> and (BSCF/AB<sub>f</sub>)<sub>centrifuged-bm</sub> electrode is less than 5%.

AB <sub>f</sub>			CF		
Peak BE	At.%		Peak BE	At.%	
284.73	63.66	C-C	284.77	76.89	C-C
285.3	11.7	C-H	287.03	4.03	C=O
286.27	11.3	C-O	285.63	13.86	C-O
288.2	4.91	C=O	291.04	5.22	satellite
290.4	4.22	COOH			
291.7	4.2	satellite			
CF <sub>bm</sub>					
Peak BE	At.%				
284.43	27.6	C-C			
285.09	30.85	C-H			
285.98	25.76	C-O			
287.5	9.01	C=O			
289.16	5.35	C=O			
290.4	1.19	COOH			
291.4	0.23	satellite			

**Table S1.** XPS-Derived Atomic Composition data for functionalized Acetylene black (AB<sub>f</sub>), Carbon fiber (CF) and Carbon fiber ball milled (CF<sub>bm</sub>).

Element	BSCF (at%)	BSCF <sub>bm</sub> (at%)
Sr	41±10	54±12
Ba	30±5	27±8
Co	23±5	15±6
Fe	5.8 ±2.5	3.7±1.9

**Table S2.** X-Ray photoelectron spectroscopy (XPS) measurements have been performed for the as prepared BSCF and for the BSCF sample after ball-milling processing. XPS measurements for BSCF oxide are particularly challenging since the main peak for Co and Ba in the XPS spectrum (Co2p and Ba3d, respectively) overlaps. Therefore, minor peaks for the Co and Ba elements have been considered, which significantly increases the error bars for the calculation of the chemical composition. Particularly, for determining the atomic ratio between the elements composing BSCF we have considered: Sr3d, Ba4d, Co3p, and Fe2p. Both samples present a significant surface enrichment in Sr, a little bit more pronounced for the treated BSCF sample. Surface Sr segregation has been already observed in other perovskite oxide presenting Sr in the A site of the ABO<sub>3</sub> perovskite structure<sup>3</sup>. However, both samples preserve the stoichiometric ratio between the Co and the Fe cations of about 4. It must be remarked that being Sr compounds (such as carbonates or hydroxide) very soluble in water, the surface composition under operative conditions might be significantly different, i.e. the dissolution of the Sr-based segregation might lead under operative conditions to a superficial enrichment in Co and Fe cations.

1 E. Fabbri, X. Cheng, Schmidt, T. J., Highly active Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> single material electrode towards the oxygen evolution reaction for alkaline water splitting applications. *Ecs Transactions* 2015, **69**, 869-875.

2 E. Fabbri, M. Nachtegaal, X. Cheng, T. J. Schmidt, Superior Bifunctional Electrocatalytic Activity of Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>-/Carbon Composite Electrodes: Insight into the Local Electronic Structure. *Adv Energy Mater* 2015, **5**, 17.

3 X. Cheng, E. Fabbri, M. Nachtegaal, I. E. Castelli, M. El Kazzi, R. Haumont, N. Marzari and T. J. Schmidt, Oxygen Evolution Reaction on La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> Perovskites: A Combined Experimental and Theoretical Study of Their Structural, Electronic, and Electrochemical properties . *Chem Mater*, 2015, **27**, 7662-7672.