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## Effect of calcium doping on the electrocatalytic activity of $Bi_{1-x}Ca_xFeO_{3-\delta}$ oxygen electrode for solid oxide fuel cells

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Fig. S1. XRD pattern of BCFx-GDC powders heated at 850 °C for 12 h.



**Fig. S2** (a) Thermogravimetric data and oxygen non-stoichiometry ( $\delta$ ) of BCF*x* between 50 and 800 °C. (b) average valences of iron for BCF*x* cathodes as a function of temperature in air.



**Fig. S3** (a) the impedance spectra of BCF0.2 cathode in different  $CO_2$  concentrations at 700 °C. (b) Short-term stability of BCF0.2 and BSF cathodes in varying amounts of  $CO_2$  at 700 °C.

**Table S1** The percentages of different Fe and O species, average valence states of Fe, and oxygen non-stoichiometry ( $\delta$ ).

Sample	Fe <sup>4+</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Average valence of Fe	δ
<i>x</i> =0.1	18.82%	68.23%	12.95%	3.058	0.021
<i>x</i> =0.2	27.26%	57.44%	15.30%	3.119	0.041
<i>x</i> =0.3	39.71%	44.03%	16.21%	3.233	0.034

**Table S2** Dependence of the capacitance and the relaxation frequency for the BCF0.2 cathode under different  $pO_2$  at 700 °C.

700 °C	$pO_2(atm)$	0.0502	0.0710	0.0901	0.1100	0.1300
HF arc	$R_{ m HF}(\Omega~{ m cm}^2)$	0.04911	0.04871	0.048511	0.04853	0.047688
	CPE <sub>HF</sub> -T (Fcm <sup>-2</sup> )	0.01493	0.01051	0.010027	0.010034	0.01746
	CPE <sub>HF</sub> -P (Fcm <sup>-2</sup> )	0.79987	0.77948	0.7712	0.77106	0.76516
	$C_{\rm HF}({\rm Fcm}^{-2})$	0.00245	0.00123	0.001042	0.001042	0.001980
	$f_{\rm HF}({\rm Fcm}^{-2})$	1320.43	2649.50	3145.632	3146.838	1684.727
LF arc	$R_{ m LF}(\Omega~{ m cm}^2)$	0.3578	0.33638	0.32834	0.30832	0.30165
	$CPE_{LF}$ -T (Fcm <sup>-2</sup> )	0.3019	0.32356	0.33846	0.33847	0.36707
	CPE <sub>LF</sub> -P (Fcm <sup>-2</sup> )	0.9186	0.90059	0.89634	0.8964	0.88116
	$C_{\rm LF}({\rm Fcm}^{-2})$	0.24786	0.25327	0.262518	0.260667	0.272803
	$f_{\rm LF}({\rm Fcm}^{-2})$	1.79457	1.86808	1.846446	1.980300	1.934048