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Figure S1. Lattice parameter variation as a function of temperature.



Figure S2. The O₂ desorption patterns of BCFSn631 and BCFNb631.



Figure S3. ECR curves (red) of BCFSn631 and BCFNb631 samples measured with reduction step from oxygen partial pressures of 0.21 to 0.1atm at different temperatures. Fitting curves (black) and deviations (blue) are also presented.



 $\label{eq:2.1} Figure S4. Oxygen permeation fluxes of BaCo_{0.7}Fe_{0.2}Sn_{0.1}O_3, \ BaCo_{0.6}Fe_{0.3}Sn_{0.1}O_3, \ and BaCo_{0.6}Fe_{0.3}Nb_{0.1}O_3.$



Figure S5. The cross-section morphology of BCFSn631 (a) and BCFNb631 (b) electrodes.



Figure S6. The I-V and I-P curves of a single cell operating with BCFNb631 cathode.

	BCFSn631		BCFNb631	
	OCV (V)	PPD (mw cm ⁻²)	OCV (V)	PPD (mw cm ⁻²)
600	0.867	1168	0.886	795
550	0.908	896	0.917	525
500	0.939	523	0.941	284
450	0.944	273	0.954	147

Table S1 Detailed OCVs and PPDs of two fuel cells (SDC electrolyte) with BCFSn631 and BCFNb631 as cathodes



Figure S7. The cross-sectional morphology of single fuel cells with BCFNb631 (a) and BCFSn631 (b) as electrodes. The topside porous layer and the bottom porous layer in the SEM image are the cathode layer and anode layer, respectively.



Figure S8. CO_2 -TPD profiles from BSCF and BCFSn631 samples after CO_2 adsorption at 650 °C for 2h with and without the presence of H₂O.

The samples are calcined in furnace in two different atmospheres at 650 °C for 2h. In one case, the samples are calcined in an atmosphere containing 5% CO₂ and 95% N₂. In the other case, to introduce H₂O, the mixed gas (5 % CO₂ and 95% N₂, 200 mL min⁻¹) is passed through a humidifier at room temperature (25 °C) before the gas is introduced into the furnace.

For the samples treated in CO₂-N₂ mixed gas without H₂O, the temperature of desorption of CO₂ starts at ~400 °C. But, the CO₂ desorption peak in BCFSn631 appears at ~900 °C, which is higher than that (~880 °C) in BSCF sample. This should be related to the much higher barium content in BCFSn631 than in BSCF and similar results were also observed in a study focused on Ba_{1-x}Sr_xCo_{0.8}Fe_{0.2}O₃ [S2]. The desorption content of CO₂ from the sample can be reflected from the area of the CO₂ desorption peak. For BCFSn631 sample treated in CO₂-N₂ mixed gas without H₂O, the area of the desorption peak is $3.67*10^{-6}$, which is slightly higher than that

 $(3.41*10^{-6})$ obtained from BSCF sample. This reveals the BCFSn631 should be more sensitive to CO₂ poisoning.

Previously, Yan et al. and Yi et al. found the presence of both H_2O and CO_2 would bring about a more serious CO_2 poisoning effect on perovskite materials, which is related to the formation of bicarbonate.[S3, S4] Herein, when H_2O is introduced into the system, the calculated areas (4.21*10⁻⁶ for BCFSn631 and 4.04*10⁻⁶ for BSCF) of CO_2 desorption peaks are higher than the samples treated in CO_2 -N₂ mixed gas without H_2O . This reveals the presence of H_2O would also aggravate the adsorption of CO_2 over BSCF and BCFSn631 sample.

References

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