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

Figure S2. The O\textsubscript{2} 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.
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.

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

<table>
<thead>
<tr>
<th></th>
<th>BCFSn631</th>
<th></th>
<th>BCFNb631</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV (V)</td>
<td>PPD (mw cm(^{-2}))</td>
<td>OCV (V)</td>
<td>PPD (mw cm(^{-2}))</td>
</tr>
<tr>
<td>600</td>
<td>0.867</td>
<td>1168</td>
<td>0.886</td>
</tr>
<tr>
<td>550</td>
<td>0.908</td>
<td>896</td>
<td>0.917</td>
</tr>
<tr>
<td>500</td>
<td>0.939</td>
<td>523</td>
<td>0.941</td>
</tr>
<tr>
<td>450</td>
<td>0.944</td>
<td>273</td>
<td>0.954</td>
</tr>
</tbody>
</table>

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 H$_2$O.

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% CO$_2$ and 95% N$_2$. In the other case, to introduce H$_2$O, the mixed gas (5 % CO$_2$ and 95% N$_2$, 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 CO$_2$-N$_2$ mixed gas without H$_2$O, the temperature of desorption of CO$_2$ starts at ~400 °C. But, the CO$_2$ 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$_x$Co$_{0.8}$Fe$_{0.2}$O$_3$ [S2]. The desorption content of CO$_2$ from the sample can be reflected from the area of the CO$_2$ desorption peak. For BCFSn631 sample treated in CO$_2$-N$_2$ mixed gas without H$_2$O, 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 CO\textsubscript{2} poisoning.

Previously, Yan et al. and Yi et al. found the presence of both H\textsubscript{2}O and CO\textsubscript{2} would bring about a more serious CO\textsubscript{2} poisoning effect on perovskite materials, which is related to the formation of bicarbonate.[S3, S4] Herein, when H\textsubscript{2}O is introduced into the system, the calculated areas (4.21*10^{-6} for BCFSn631 and 4.04*10^{-6} for BSCF) of CO\textsubscript{2} desorption peaks are higher than the samples treated in CO\textsubscript{2}-N\textsubscript{2} mixed gas without H\textsubscript{2}O. This reveals the presence of H\textsubscript{2}O would also aggravate the adsorption of CO\textsubscript{2} over BSCF and BCFSn631 sample.

References