Figure S1. XRD patterns of $\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\!\_\delta$ with $x > 1.00$ recorded after calcined at 1000 $^\circ$C for 5 h and exposed in ambient air for 20 min (Relative Humidity = (70 ± 2) %).

For $\text{Sr}_{1.05}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\!\_\delta$, the max diffraction peak at 29.1$^\circ$ is corresponding to an unknown phase and another visible diffraction peak appears at 6.2$^\circ$. The unknown phase just present in $\text{Sr}_{1.05}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\!\_\delta$ may be $\text{SrCoO}_4$ (PDF# 44-1064), but it is not sure because only two diffraction peaks can be identified. Furthermore, for $\text{Sr}_{1.10}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\!\_\delta$ and $\text{Sr}_{1.20}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\!\_\delta$, the peak at $2\theta = 29.1^\circ$ disappears but the diffraction peak of 6.2$^\circ$ gets stronger, which correspond to the moisture-sensitive phase $\text{Sr}_3(\text{Co, Fe})_2\text{O}_7\!\_\delta$ (space groupI4/mmm) not $\text{Sr}_2(\text{Co, Fe})_4\text{O}_{10\!\_\delta}$ or $\text{Sr}_4(\text{Co, Fe})_3\text{O}_{10\!\_\delta}$, in respect that $\text{Sr}_2(\text{Co, Fe})_4\text{O}_{10\!\_\delta}$ and $\text{Sr}_4(\text{Co, Fe})_3\text{O}_{10\!\_\delta}$ are stable only at low temperatures. Exposed to ambient air just for 20 min, there is $\text{Sr}_3(\text{Co, Fe})_2\text{O}_7\!\_\delta\cdot2\text{H}_2\text{O}$ in samples $\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\!\_\delta$ ($x = 1.05, 1.00$ and $1.20$), which agree with the results about $\text{Sr}_3\text{Fe}_2\text{O}_7\!\_\delta$ in the literature. Water molecular is prone to insert two neighbor layers of $\text{Sr}_3(\text{Co, Fe})_2\text{O}_7\!\_\delta$ to form $\text{Sr}_3(\text{Co, Fe})_2\text{O}_7\!\_\delta\cdot2\text{H}_2\text{O}$, and then the volume of the material expands.
Figure S2. Cross-section of Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ sintered at 1100 °C for 5 h in air.

Note that the A-site cation excess pellets were quickly taken from 150 °C oven to the SEM chamber in order to minimize the adsorption of water molecular from ambient air.

It is seen that the relative density decreases with increasing of $x$, similar to the variation of (Ba$_{0.5}$Sr$_{0.5}$)$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ reported in literature.$^3$ Such a behavior was attributed to an increased concentration of the A-site vacancies which enhanced the diffusion of the A-site cations during the sintering. The cobalt-iron oxide in
Sr$_{0.80}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ is a sintering aid to enhance the densification of samples. However, under-sintering behavior appeared in Sr$_{1.05}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$, Sr$_{1.10}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ and Sr$_{1.20}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$. It implies that Sr$_3$Fe$_2$O$_7$-$\delta$ is a sintering barrier causing the relative density decreasing.

![Figure S3](image)

**Figure S3** Temperature dependence of the polarization resistance of various Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ cathodes in air.

Arrhenius plots of the polarization resistances of electrodes are shown in Figure S3 obtained from results of Figure 4b in text. The activation energy $E_a$ is corresponding to the energy of the oxygen reduction reactions. Note that the polarization process is related to the rate of the oxygen reduction reactions, which can be affected by $E_a$ and pre-exponential factor. From $x$ of 1.20 to 0.80, the values of $E_a$ for $x > 1.00$ are totally smaller than the ones for $x \leq 1.00$, although the polarization resistances for $x > 1.00$ are obviously bigger than the ones for $x \leq 1.00$. $E_a$ of Sr$_{1.20}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ is equal to 0.82 eV while $E_a$ of Sr$_{1.00}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ is as higher as 1.16 eV. However, the polarization resistances of Sr$_{1.20}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ are several times bigger than the values of Sr$_{1.00}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ during operating temperatures. It is clear that for the rate of oxygen surface exchange, $E_a$ is one of the primary factors but not the only one.
Figure S4. Cell voltage and power density as a function of current density at various temperatures obtained on Ni-SDC supported SDC electrolyte with a cathode of SrₓCo₀.₈Fe₀.₂O₃₋δ (x = 0.80 - 1.20), and Impedance spectra for the single cells with cathode SrₓCo₀.₈Fe₀.₂O₃₋δ. Air was supplied to the cathode side (300 ml min⁻¹ at STP) and humidified H₂ (3 vol. % H₂O) was supplied to the anode side (100 ml min⁻¹ at STP). A voltage amplitude of 10 mV was applied for AC impedance spectroscopy in the frequency range from 10² Hz to 10⁵ Hz.
References

