Supplementary Material (ESI) for Energy & Environmental Science

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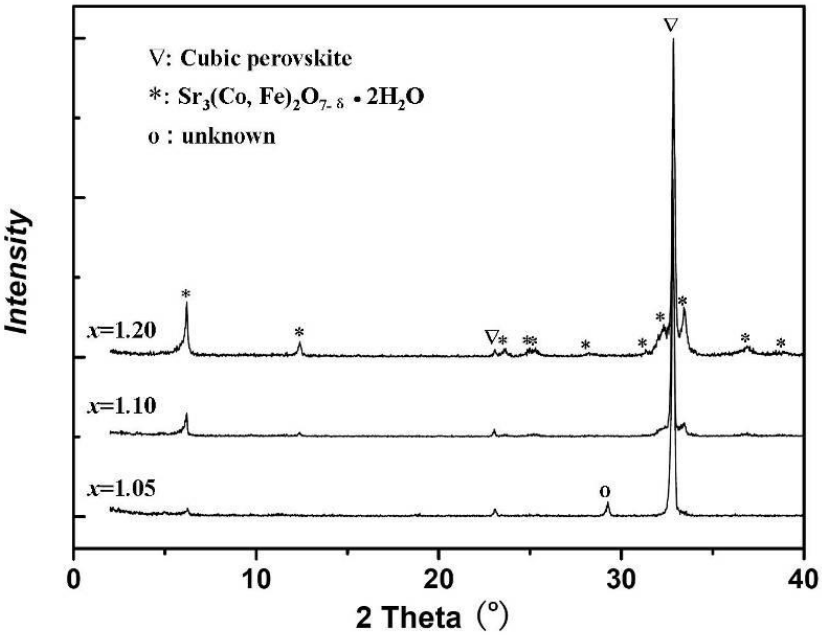


Figure S1. XRD patterns of $Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ with $x > 1.00$ recorded after calcined at 1000 °C for 5 h and exposed in ambient air for 20 min (Relative Humidity = (70 ± 2) %).

For $Sr_{1.05}Co_{0.8}Fe_{0.2}O_{3-\delta}$, the max diffraction peak at 29.1° is corresponding to an unknown phase and another visible diffraction peak appears at 6.2°. The unknown phase just present in $Sr_{1.05}Co_{0.8}Fe_{0.2}O_{3-\delta}$ may be $SrCoO_x$ (PDF#: 44-1064), but it is not sure because only two diffraction peaks can be identified. Furthermore, for $Sr_{1.10}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $Sr_{1.20}Co_{0.8}Fe_{0.2}O_{3-\delta}$, the peak at $2\theta = 29.1°$ disappears but the diffraction peak of 6.2° gets stronger, which correspond to the moisture-sensitive phase $Sr_3(Co, Fe)_2O_{7-\delta}$ (space groupI4/mmm) not $Sr_2(Co, Fe)O_{4-\delta}$ or $Sr_4(Co, Fe)_3O_{10-\delta}$, in respect that $Sr_2(Co, Fe)O_{4-\delta}$ and $Sr_4(Co, Fe)_3O_{10-\delta}$ are stable only at low temperatures.[1] Exposed to ambient air just for 20 min, there is $Sr_3(Co, Fe)_2O_{7-\delta}\cdot 2H_2O$ in samples $Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ (x = 1.05, 1.00 and 1.20), which agree with the results about $Sr_3Fe_2O_{7-\delta}$ in the literature.[2] Water molecular is prone to insert two neighbor layers of $Sr_3(Co, Fe)_2O_{7-\delta}$ to form $Sr_3(Co, Fe)_2O_{7-\delta}\cdot 2H_2O$, and then the volume of the material expands.

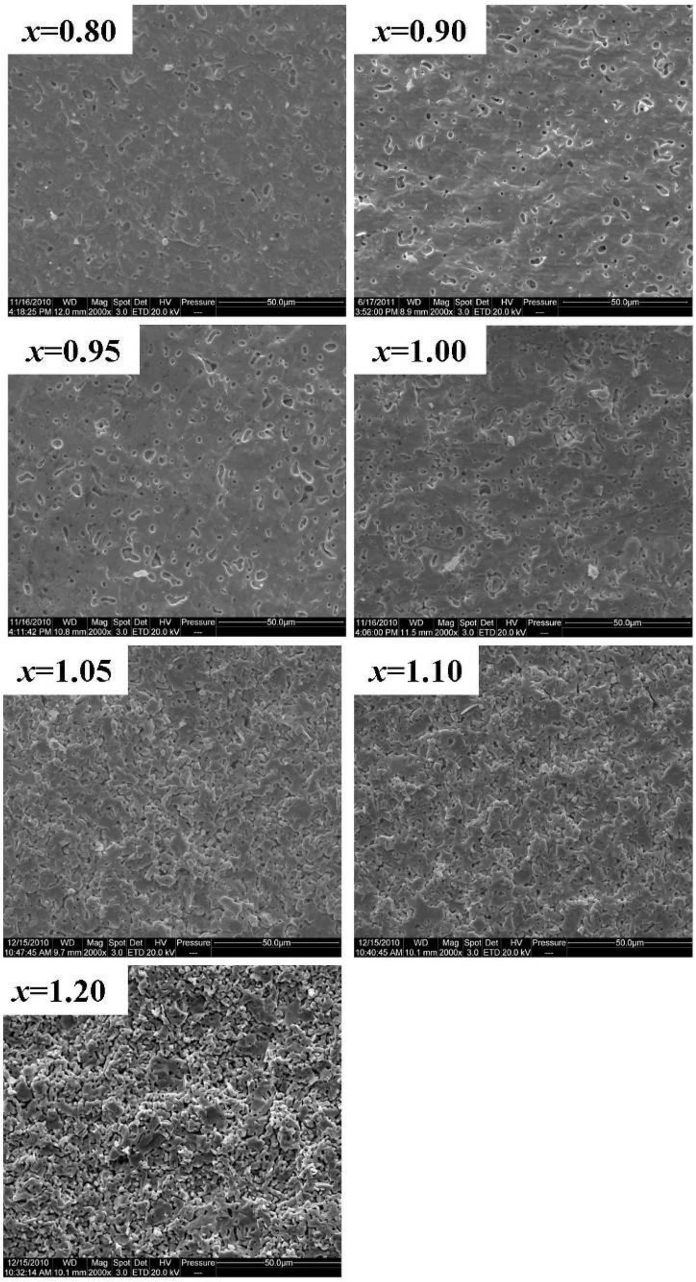


Figure S2. Cross-section of $Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ sintered at 1100 ^{o}C for 5 h in air.

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 $Sr_3Fe_2O_{7-\delta}$ is a sintering barrier causing the relative density decreasing.

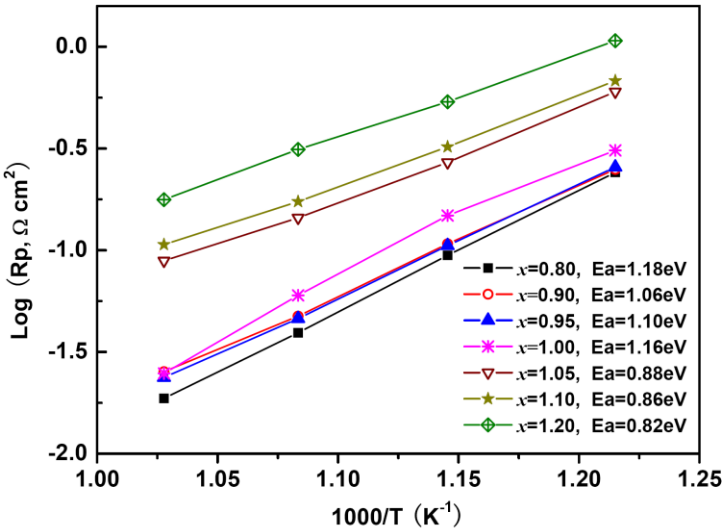
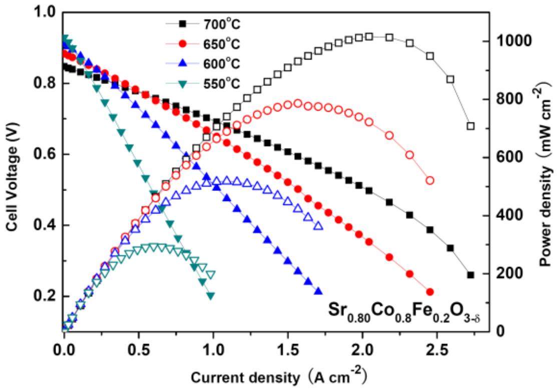
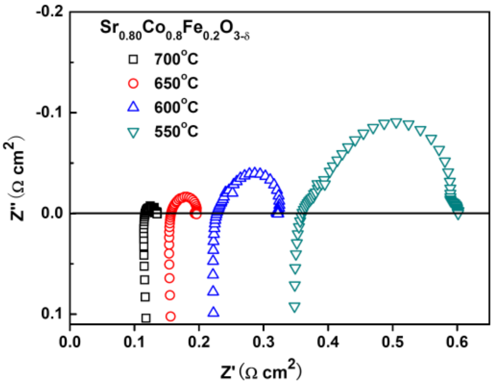
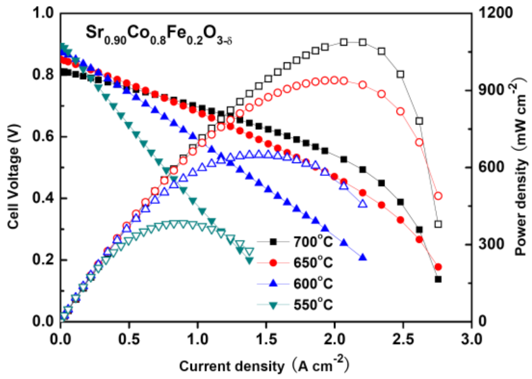


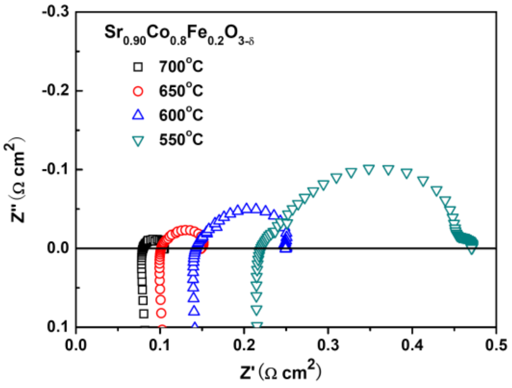
Figure S3 Temperature dependence of the polarization resistance of various $Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ cathodes in air.

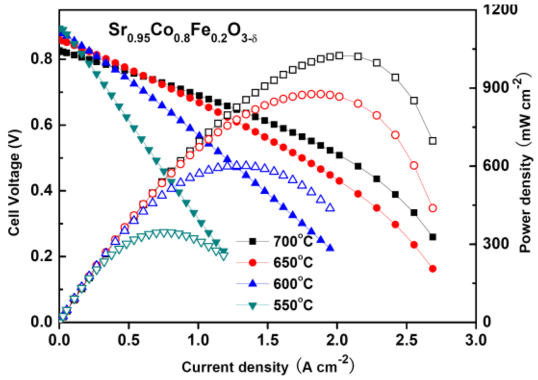
Arrhenius plots of the polarization resistances of electrodes are shown in Figure S3 obtained from results of Figure 4b in text. The activation energy *E*a is corresponding to the energy of the oxygen reduction reactions. Note that the polarization process is related to the rate of the oxygen reduction 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, Ea is one of the primary factors but not the only one.

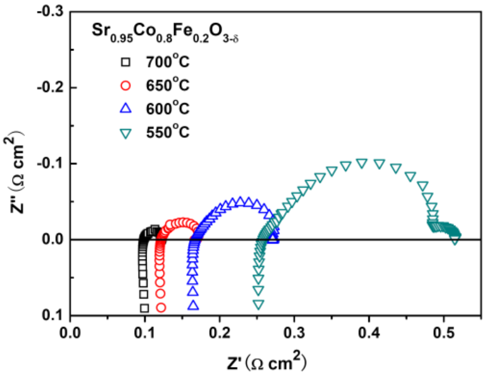

700°C
650°C
600°C
550°C
$Sr_{0.80}Co_{0.8}Fe_{0.2}O_{3-\delta}$
Cell Voltage (V)
1.0
0.8
0.6
0.4
0.2
Power density (mW cm^{-2})
1000
800
600
400
200
0
Current density (A cm^{-2})
0.0
0.5
1.0
1.5
2.0
2.5

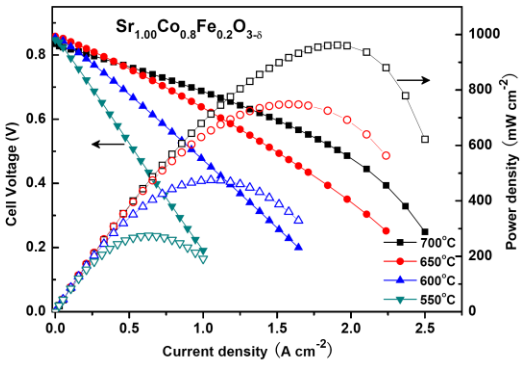

$Sr_{0.80}Co_{0.8}Fe_{0.2}O_{3-\delta}$
700°C
650°C
600°C
550°C
Z'' (Ω cm^2)
-0.2
-0.1
0.0
0.1
Z' (Ω cm^2)
0.0
0.1
0.2
0.3
0.4
0.5
0.6

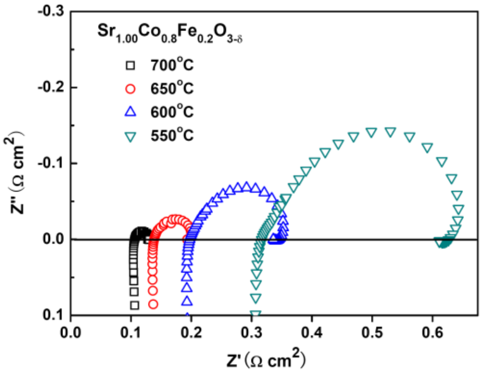

$Sr_{0.90}Co_{0.8}Fe_{0.2}O_{3-\delta}$
700°C
650°C
600°C
550°C
Cell Voltage (V)
1.0
0.8
0.6
0.4
0.2
0.0
Power density (mW cm^{-2})
1200
900
600
300
0
Current density (A cm^{-2})
0.0
0.5
1.0
1.5
2.0
2.5
3.0


$Sr_{0.90}Co_{0.8}Fe_{0.2}O_{3-\delta}$
700°C
650°C
600°C
550°C
Z'' (Ω cm^2)
-0.3
-0.2
-0.1
0.0
0.1
Z' (Ω cm^2)
0.0
0.1
0.2
0.3
0.4
0.5


$Sr_{0.95}Co_{0.8}Fe_{0.2}O_{3-\delta}$
700°C
650°C
600°C
550°C
Cell Voltage (V)
0.8
0.6
0.4
0.2
0.0
Power density (mW cm^{-2})
1200
900
600
300
0
Current density (A cm^{-2})
0.0
0.5
1.0
1.5
2.0
2.5
3.0


$Sr_{0.95}Co_{0.8}Fe_{0.2}O_{3-\delta}$
700°C
650°C
600°C
550°C
Z'' (Ω cm^2)
-0.3
-0.2
-0.1
0.0
0.1
Z' (Ω cm^2)
0.0
0.1
0.2
0.3
0.4
0.5


$Sr_{1.00}Co_{0.8}Fe_{0.2}O_{3-\delta}$
700°C
650°C
600°C
550°C
Cell Voltage (V)
0.8
0.6
0.4
0.2
0.0
Power density (mW cm^{-2})
1000
800
600
400
200
0
Current density (A cm^{-2})
0.0
0.5
1.0
1.5
2.0
2.5


$Sr_{1.00}Co_{0.8}Fe_{0.2}O_{3-\delta}$
700°C
650°C
600°C
550°C
Z'' (Ω cm^2)
-0.3
-0.2
-0.1
0.0
0.1
Z' (Ω cm^2)
0.0
0.1
0.2
0.3
0.4
0.5
0.6

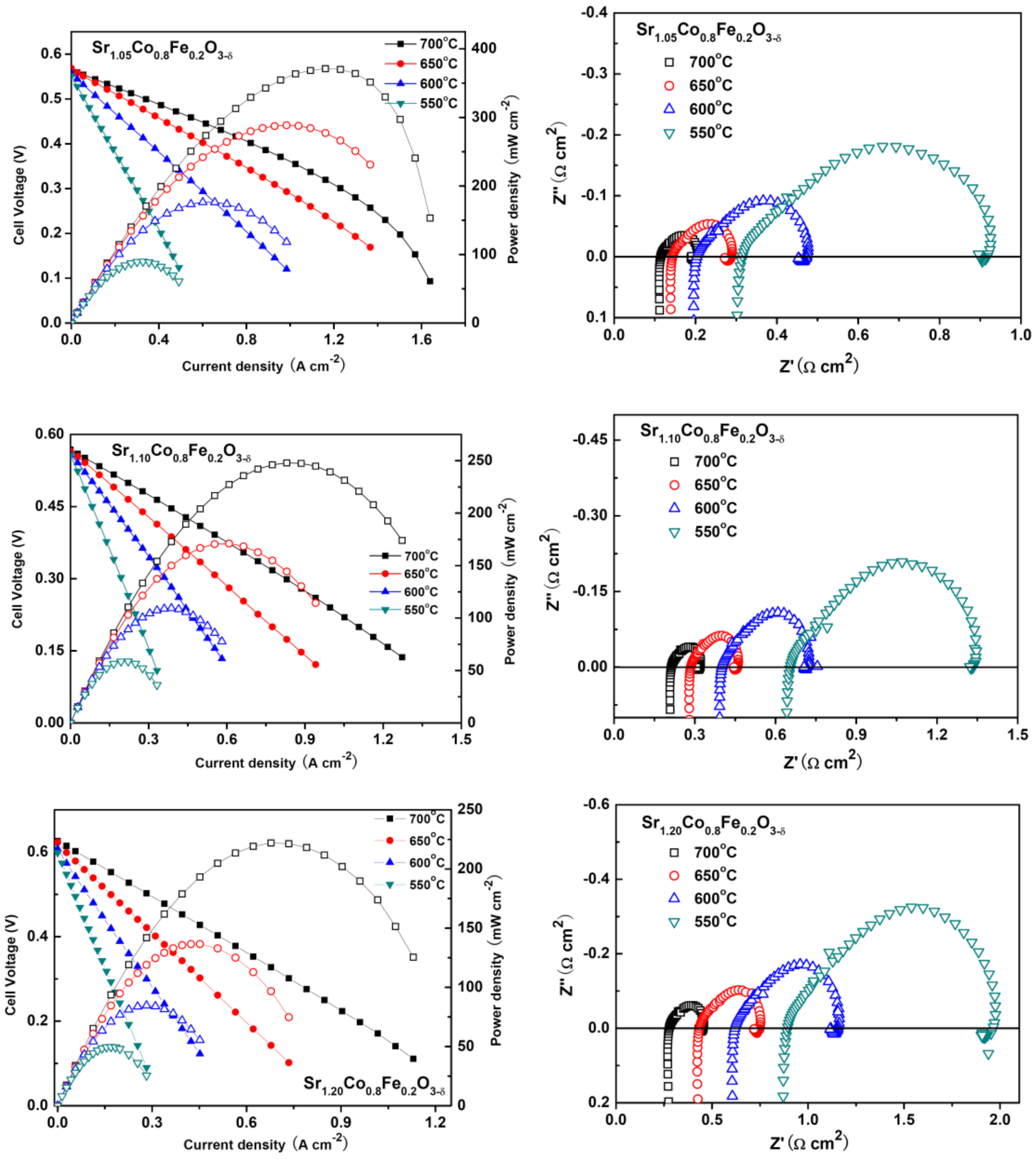


Figure S4. Cell voltage and power density as a function of current density at various temperatures obtained on Ni-SDC supported SDC electrolyte with a cathode of $Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ (x = 0.80 - 1.20), and Impedance spectra for the single cells with cathode $Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$. Air was supplied to the cathode side (300 ml min^{-1} at STP) and humidified H_2 (3 vol. % H_2O) 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 10^{-2} Hz to 10^{5} Hz.

References

1. M. Lehtimäki, A. Hirasa, M. Matvejeff, H. Yamauchi and M. Karppinen, *J. Solid State Chem.*, 2007, **180**, 3247–3252.
2. M. Matvejeff, M. Lehtimäki, A. Hirasa, Y.-H. Huang, H. Yamauchi and M. Karppinen, *Chem. Mater.*, 2005, **17**, 2775–2779.
3. L. Ge, W. Zhou, R. Ran, S. M. Liu, Z. P. Shao, W. Q. Jin and N. P. Xu, *J. Membr. Sci.*, 2007, **306**, 318–328.