Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

1. The PDOS of Co neighbouring dopants to Nb and Ta

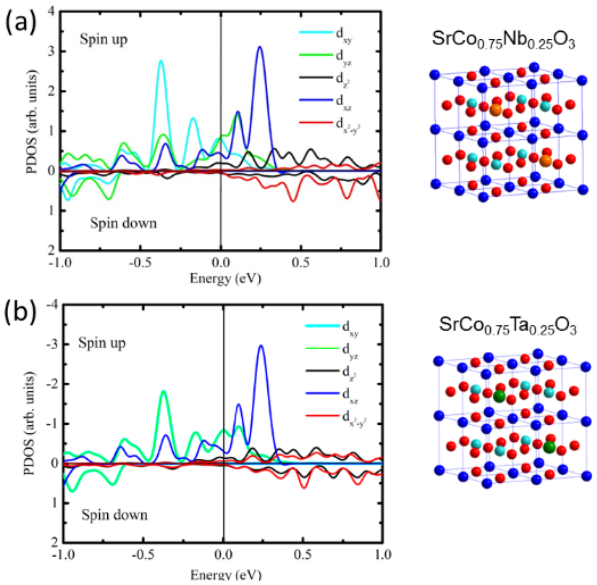

Figure S1 Atomic orbital resolved electron density (PDOS) projected on the nearest Co atoms to Nb or Ta in (a) SCN20 and (b) Ta respectively.

2. SEM images for SCN20 and SCT20 powders following TGA

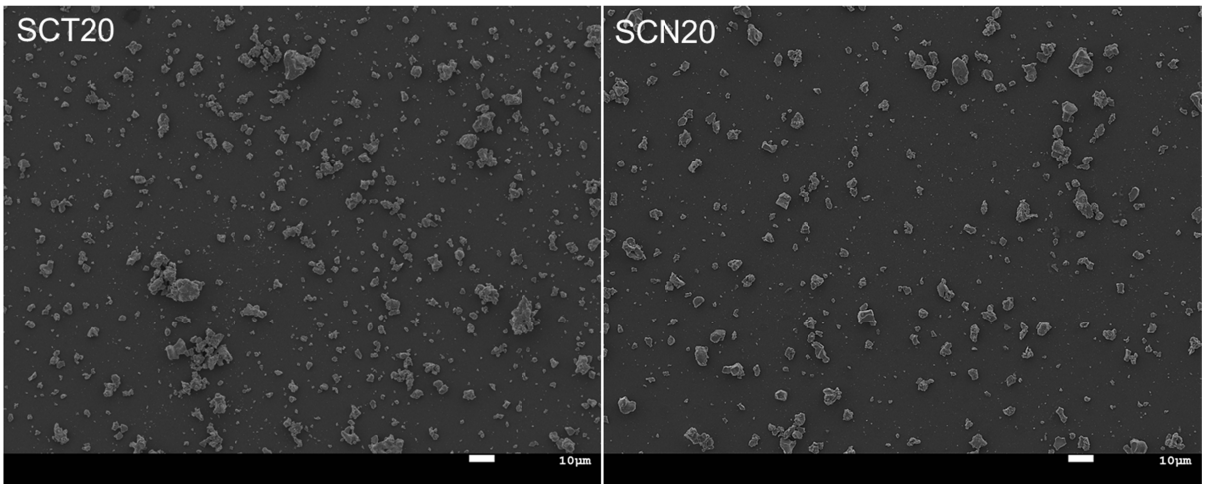

Figure S2. SEM images of the SCT20 and SCN20 powders following TGA.

3. Electrical conductivities of SCN20 and SCT20

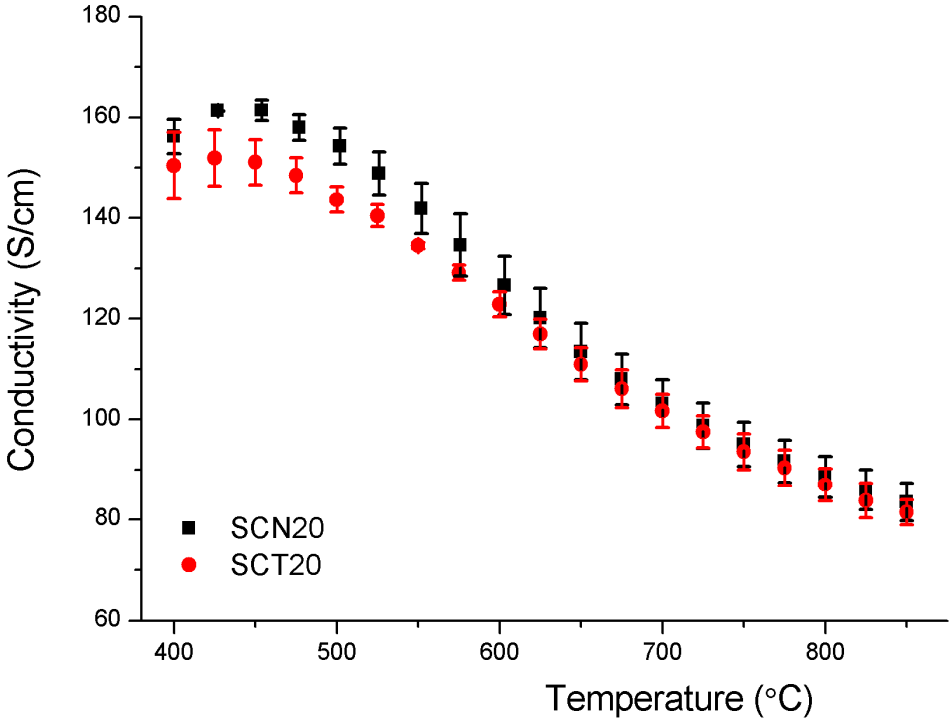

Figure S3. Electrical conductivities of SCN20 and SCT20 as a function of temperature ranging from 375 to 850 °C.

Electrical conductivities of SCN20 and SCT20 were studied by 4-probe conductivity testing at variable temperature (375 -850 °C) in flowing air. Both SCN20 and SCT20 show gradually decreasing electrical conductivities with rising temperature above 400 °C, indicating metallic conductor behavior.

4. Chemical compatibilities of SCN20 and SCT20 cathodes with SDC electrolyte

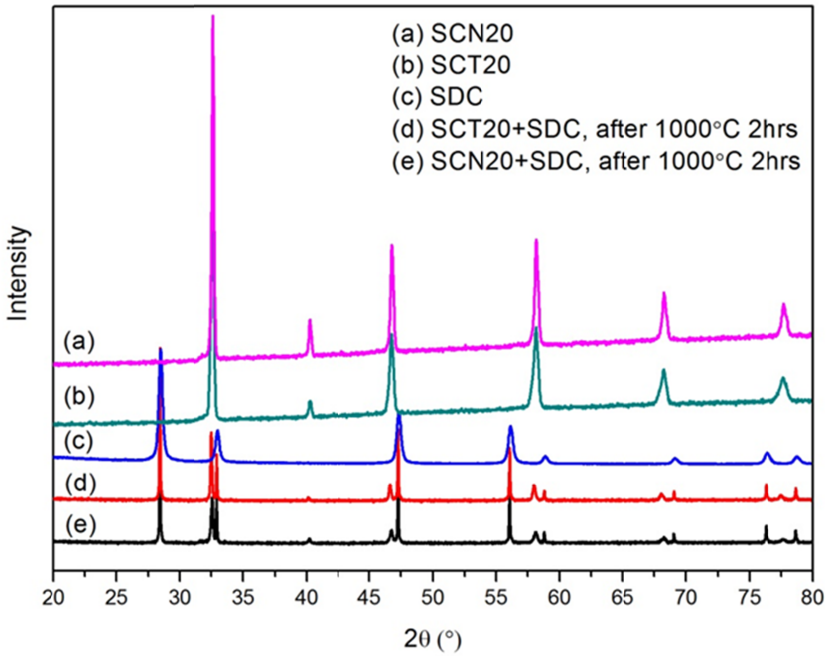

Figure S4. XRD (Cu K_α) pattens of SCN20, SCT20, and SDC at room temperature, and SCT20 and SCN20 well mixed with SDC respectively followed by pelletising and sintering at 1000 °C for 2 hours.

The compatibilities of SCN20 and SCT20 with the electrolyte $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) was investigated by comparing the crystallite structures of the cathode materials, SDC, and the powders prepared by well mixing the cathode and SDC powders (50:50 wt.%) followed by sintering at 1000 °C for 2 h. XRD patterns indicate that no reaction occurred between SDC and SCN20 or SCT20 powders at 1000 °C, which is the fabrication temperature of the cathodes. Therefore, it can be concluded that both SCN20 and SCT20 exhibit excellent chemical compatibilities with SDC powders.

5. Cross sections of SCN20 and SCT20 membranes

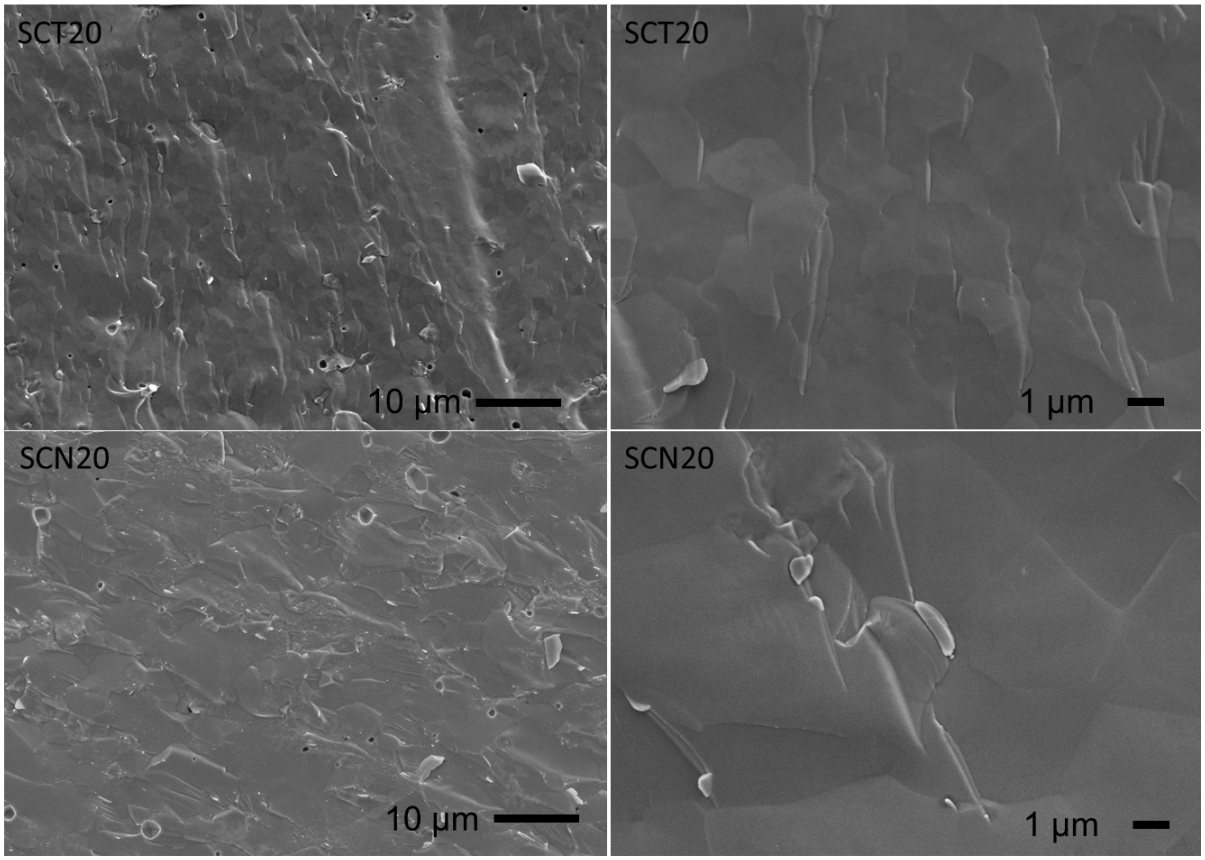

Figure S5. SEM cross sectional images of membranes for oxygen permeability tests, showing relative dense samples for both SCN20 and SCT20, and slight larger grain size of SCN20 (~4μm) than SCT20(~3μm).

6. Ionic conductivity estimation

The ionic conductivity of SCN20 and SCT20 was determined by studying the oxygen permeation of both materials as a function of temperature between 700 and 850 °C. The overall resistance to oxygen permeation through the ceramic membrane can be obtained from the following equation[1]:

$$R_{overall} = \frac{RT}{16F^2}\frac{1}{SJ_{O_2}}[\ln\left(\frac{P'_{O_2}}{P''_{O_2}}\right)]$$

R - the ideal gas constant
F - the Faraday constant
S - the valid area of the membrane
J_{O_2}- the oxygen permeation flux
P'_{O_2} - The oxygen partial pressure at the side of membrane exposed to air
P''_{O_2} - the oxygen partial pressure at the sweep side

If the oxygen permeation process is dominated by the bulk diffusion, the resistance from ionic conduction will become the major contribution to the overall permeation resistance. Therefore, the overall resistance is controlled by ionic conduction and ionic conductivity can be estimated by the following equation:

$$\sigma_{ionic} = \frac{1}{R_{ionic}} \times \frac{S}{L} \approx \frac{1}{R_{overall}} \times \frac{S}{L}$$

Where L is the thickness of the membrane.
The thickness of the membrane is far larger than the characteristic length L_c, which is the ratio between the oxygen diffusivity and the surface exchange coefficient. L_c, obtained from the results of ECR experiments, is around 0.0084-0.0178 cm for SCN20 and 0.016-0.022 cm for SCT20, while the thickness of both membranes is 0.069 cm. Therefore, it is reasonable to assume that bulk diffusion is the predominate process of the oxygen permeation

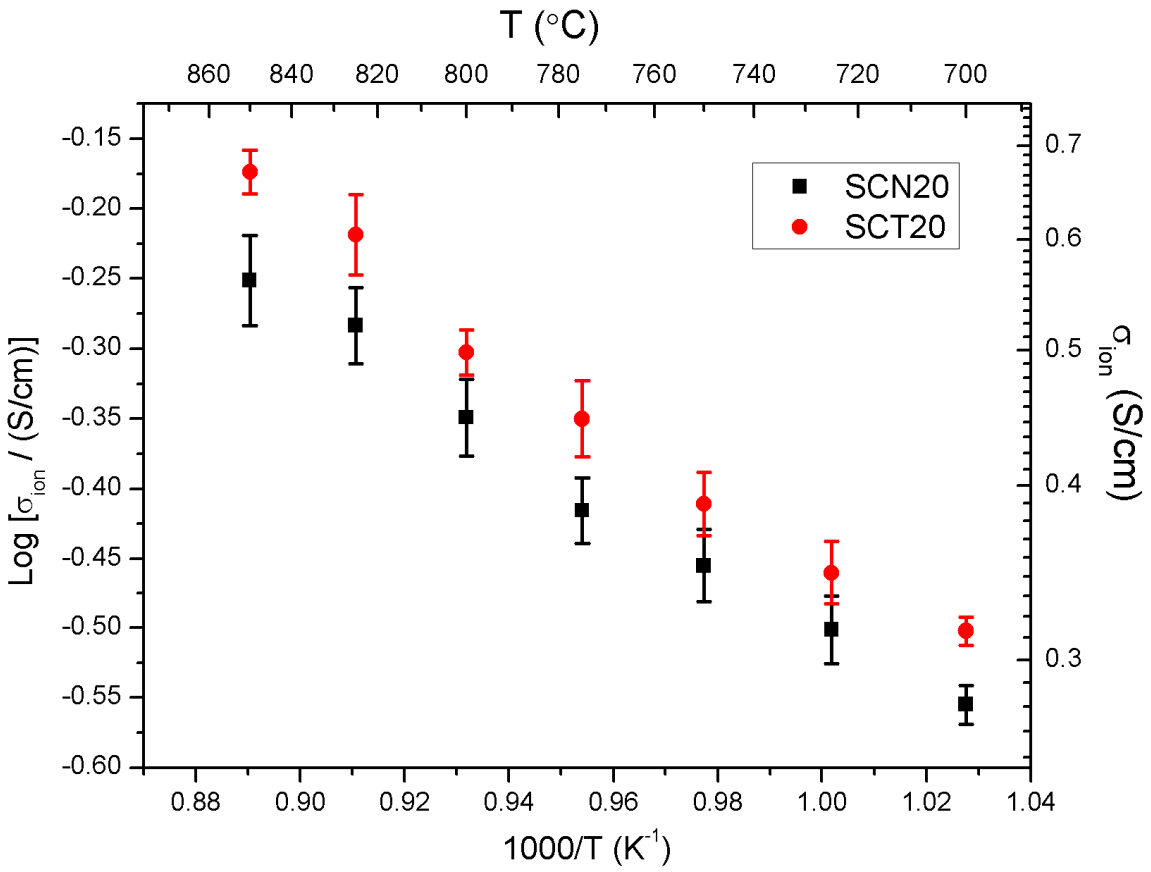

Figure S6. Comparison of ionic conductivities for SCN20 and SCT20 estimated by studing the oxygen permeabilities against temperature.

7. Electrical impedance spectroscopy

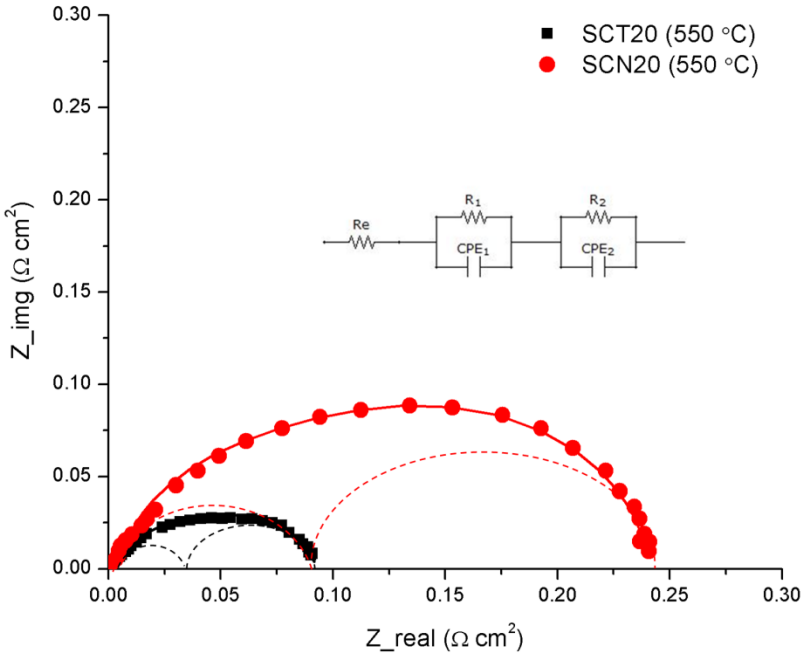

Figure S7. An example of equvialent circuit fitting of EIS data for SCN20 and SCT20 cathodes at 550 °C.

Table S1. ASR values corresponding to different processes (low frequency = LF, high frequency = HF).

Temperature(°C)	SCN20 (Ω·cm^2)		SCT20(Ω·cm^2)	
	ASR-HF	ASR-LF	ASR-HF	ASR-LF
500	0.36	0.41	0.12	0.14
550	0.092	0.15	0.036	0.057
600	0.017	0.07	0.014	0.021
650	0.0065	0.029	0.006	0.011

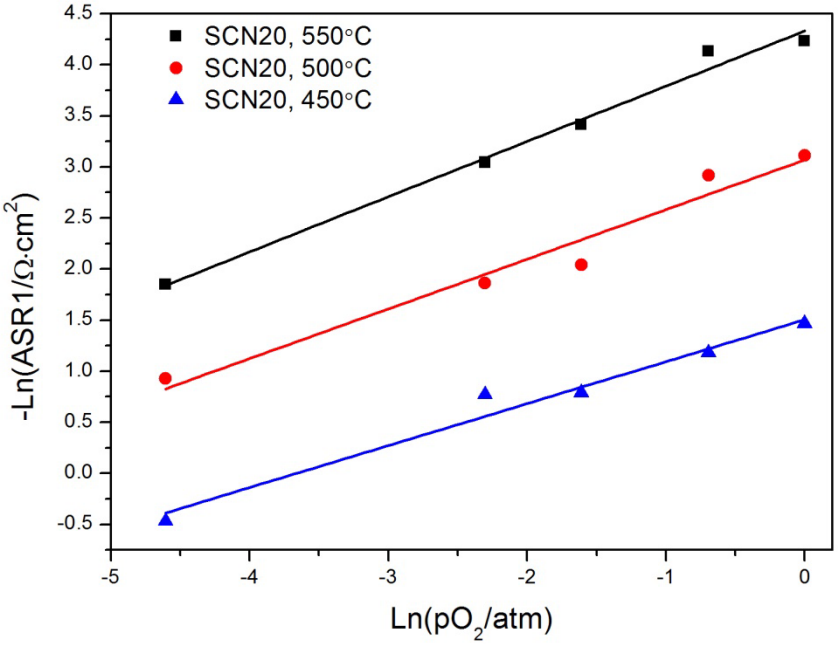

Figure S8. ASR values of the SCN20 cathode corresponding to the process at low frequencies at different temperatures against the oxygen partial pressure.

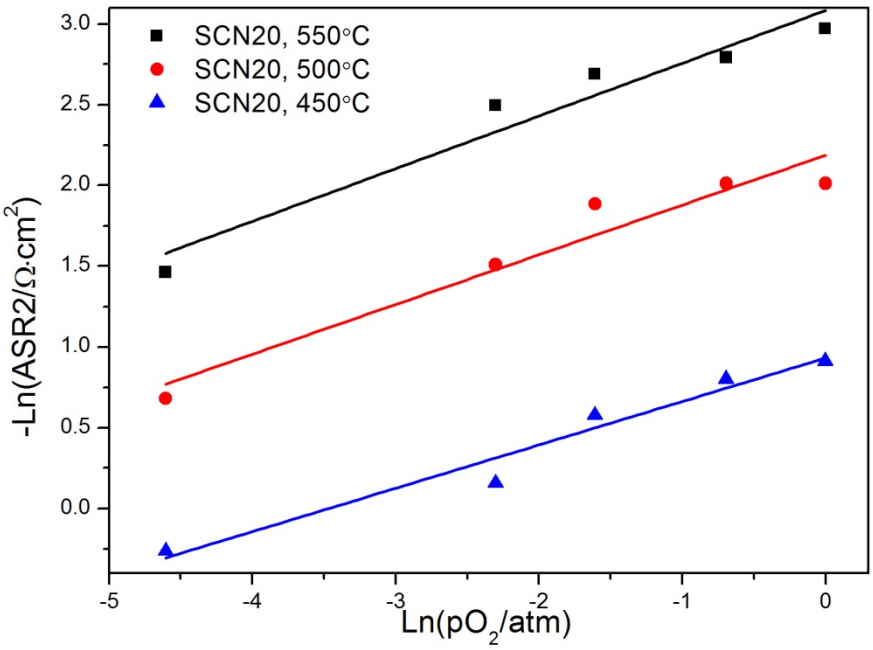

Figure S9. ASR values for the SCN20 cathode corresponding to the process at high frequencies at different temperatures against the oxygen partial pressure.

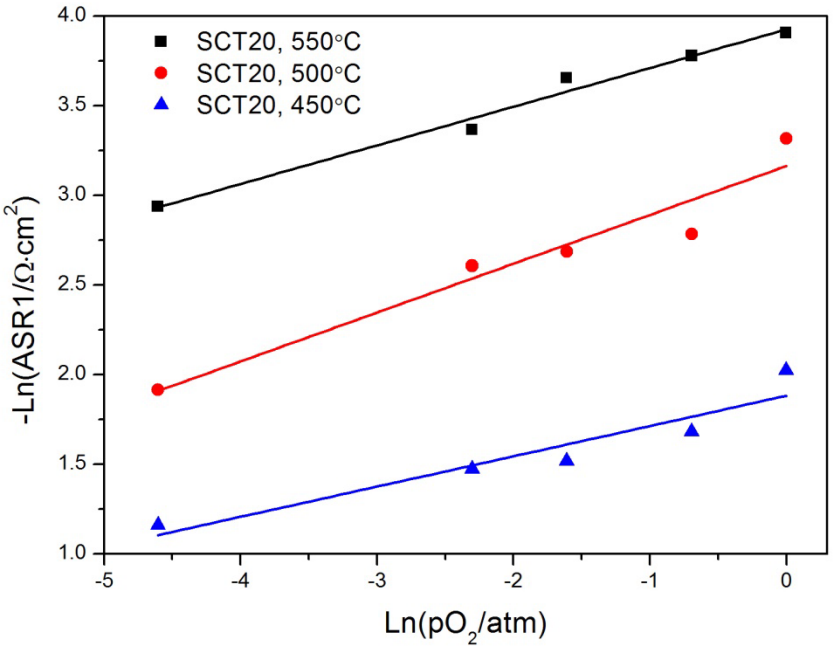

Figure S10. ASR values for the SCT20 cathode corresponding to the process at low frequencies at different temperatures against the oxygen partial pressure.

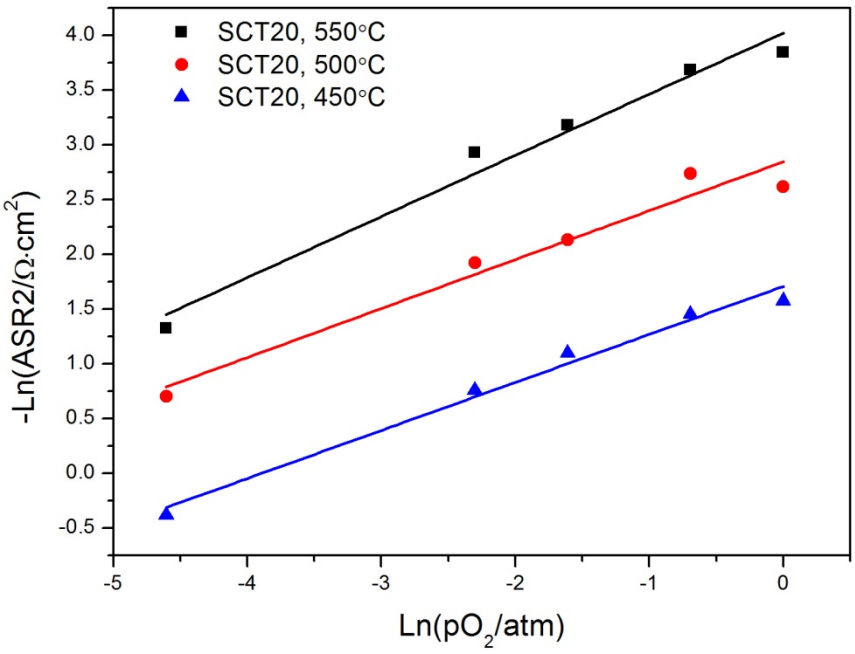

Figure S11. ASR values for the SCT20 cathode corresponding to the process at high frequencies at different temperatures against the oxygen partial pressure.

The mechanism of ORR was studied by measuring the resistances of target cathode materials at different oxygen partial pressures over the temperature range 450 -550 °C. Electrical impedance spectra were fitted to the Re(R1Q1)(R2Q2) equivalent circuit model using LEVM software, where Re represents the ohmic resistance of the SDC electrolyte, and the two series connected elements (RQ) correspond to two ORR processes: the R is the resistance and Q is the constant phase element.

The parameter that usually determines the ORR is the slope of electrode resistance against the temperature as provide by the following relationship[2]:

$$\frac{1}{R_p} \propto P_{O_2}^m$$

As shown in the above figures, the slope of ASR at low frequencies (ASR-LF) is 0.14-0.19 for SCN20 and 0.17-0.22 for SCT20, while the slope of ASR at high frequencies (ASR-HF) is 0.35-0.4 for SCN20 and 0.44-0.56 for SCT20. The slope of the ASR-HF for both of SCN20 and SCT20 is close to 0.25, implying that the first step was limited by the following process[2]:

$$O_{2,ads} + 2e' + V_O^{\cdot\cdot} \Leftrightarrow O_o^x$$

$O_{2,ads}$ denotes an oxygen molecule absorbed onto the cathode surface;
e' is an electron;
$V_O^{\cdot\cdot}$ represents an oxygen vacancy with a double positive charge;
O_o^x is an oxygen occupying an oxygen lattice site with a neutral charge.

The slope for the second process for both of cathodes is close to 0.5, which indicates that non-charge transfer dominates.

Reference

1. P. Zeng, Z. Chen, W. Zhou, H. Gu, Z. Shao and S. Liu, *Journal of Membrane Science*, 2007, **291**, 148-156.
2. Y. Takeda, R. Kanno, M. Noda, Y. Tomida and O. Yamamoto, *Journal of The Electrochemical Society*, 1987, **134**, 2656-2661.