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Supporting information

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The electrical conductivity of SFO sample was studied using a four-probe direct current (DC) technique. For the conductivity measurement, the SFO powders were pressed into a rectangular bar of approximately0.075cm in height, 4.0cm in length, and 0.67cm in width, and then sintered at 1225 °C for 10 hrs in air to form dense samples. Four silver wires were used as the current collectors with silver paste applied to improve the contact between the wires and the SFO samples. As shown in Fig.S1, the electrical conductivities of the sintered Sr₃Fe₂O_{7- δ} (SFO) increase first with the increasing testing temperature and then decrease. Maximum conductivity is achieved

at 500°C with the value of 60 Scm⁻¹, which is lower than those of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}(\sim 400Scm^{-1})^1$ and $La_{0.65}Sr_{0.3}MnO_{3-\delta}(100Scm^{-1})^2$ cathodes, but higher than that of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode (about 28.1Scm⁻¹ at 500°C)³, and meets the requirement for the cathodic application in SOFC.



Figure S1. The conductivity of $Sr_3Fe_2O_{7-\delta}$ at different temperatures measured

in air

The oxygen permeation flux through a dense $Sr_3Fe_2O_{7-\delta}$ disk sintered at 1225 °C for 10 hrs was characterized to demonstrate the possible oxygen ion conductivities. Oxygen permeation measurement was performed by exposing one side of the SFO disk (1.12mm in thickness) to the flowing air and the other side to a sweep gas of high purity helium at a sweeping rate of 10 sccm. As shown in Fig.S2, oxygen permeation flux increases with the measured temperatures. At 800 °C, the oxygen flux through SFO disk was $6.06*10^{-8}$ molcm⁻²s⁻¹, close to that of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- $\delta}$ (~12*10⁻⁸ molcm⁻²s⁻¹)⁴, suggesting good oxygen ion conductivity of SFO.}



Fig.S2. Temperature dependence of the oxygen permeation rate of

Sr₃Fe₂O_{7-δ}. The thickness of SFO disk is 1.12mm.

Electrical conductivity relaxation (ECR) was adopted to get the surfaceexchange coefficient of SFO. For the ECR experiment, the sample was sealed in a quartz tube with a flow of O_2/N_2 mixture at a rate of 300 ml*min⁻¹ to minimize the time for gas equilibrium. After the sample reached equilibrium at the testing temperature, the oxygen partial pressure changed abruptly from 0.01 atm to 0.21 atm. Electrical conductivity relaxation (ECR) test was conducted by measuring the conductivity change in the abrupt process until a new balance was established. The time dependences of the normalized conductivity for $Sr_3Fe_2O_{7-\delta}$ (SFO) when P_{O_2} changing abruptly from 0.01 to 0.21 atm are shown in Fig. S3 measured at various temperatures. Considering the process is absolutely surface-controlled, exchange coefficients of oxygen (k) can be obtained from the curve fitting procedure using the equation (1)⁵.

$$n(t) = 1 - \exp(\frac{-1}{d/2}Kt) \tag{1}$$

The fitted exchange coefficients of SFO are $3.45*10^{-4}$, $1.8*10^{-4}$, $9.80*10^{-5}$ and $4.80*10^{-5}$ cms⁻¹measured at 800, 750, 700 and 650 °C, respectively. The activation energy for surface exchange reaction is approximately 1.11 eV. The exchange coefficients are higher than that of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- $\delta}$} (0.89*10⁻⁵ cms⁻¹ at 700°C)⁶.



Fig.S3.Conductivity data of Sr₃Fe₂O_{7-δ} versus time over the gas switching O₂/N₂ (1:99) to O₂/N₂ (21:79) at various temperatures (a); and the temperature dependence of surface exchange coefficient (K) for Sr₃Fe₂O_{7-δ} (b)



Fig.S4. BZCY content dependence of the ohmic resistance (Ro) and the polarization resistance (Rp) of the single cells determined from the impedance spectra at $650 \,^{\circ}$ C



Fig.S5. Experimental and fit Nyquist plots in atmosphere consisting of

 $0.05^{*}10^{5}$ Pa $H_{2}O$ and $0.21^{*}10^{5}$ Pa O_{2} at $600^{\circ}C$



Fig.S6. The SEM image of the tested cell with the structure of Ni-BZCY|BZCY|SFO-5wt.%BZCY

The calculated surface energies of SFO with different terminated surface indicated in Fig.S7 are shown in Table S1. The (001)-3, representing the Rock-Salt SrO surface, is the most stable surface with the lowest energy of 0.49 J^*m^{-2} .

Table.S1. Summary of calculated surface energies of SFO with different

terminated surface. The numbers here denote different terminated surface as

shown	in Fig.S7.	

Surface	100	110	111	011	001-1	001-2	001-3
E/J*m⁻²	0.92	1.38	1.36	1.44	0.91	1.19	0.49



Fig.S7. The different terminated surface of $Sr_3Fe_2O_{7-\delta}$ oxide.

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