Supporting Material for

Highly active and stable $(La_{0.24}Sr_{0.16}Ba_{0.6})(Co_{0.5}Fe_{0.44}Nb_{0.06})O_{3-\delta}$ (LSBCFN) cathode for solid oxide fuel cells by a novel mixing synthesis method

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Support Information:

Fig.S1 shows the impedance and polarization curves of the LSCF, BCFN and LSBCFN electrode at 900°C under a current passage of 200 mA cm^{-2} in the absence of the metallic interconnect. A gradual decrease in R_Ω was detected and it could be related to the improved contact between the electrode and the electrolyte under the current passage at the high temperature. Different from the obvious activation effects observed at pure electronic conductors like $(La,Sr)MnO_{3\pm\delta}$, the electrodes studied show more or less stable R_E and η values during the current passage, an characteristic of the mixed ionic and electronic conducting oxide electrodes[1]. It indicated that the electrochemical performance of the LSCF, BCFN and LSBCFN electrode were stable under the current passage in the absence of the metallic interconnect.
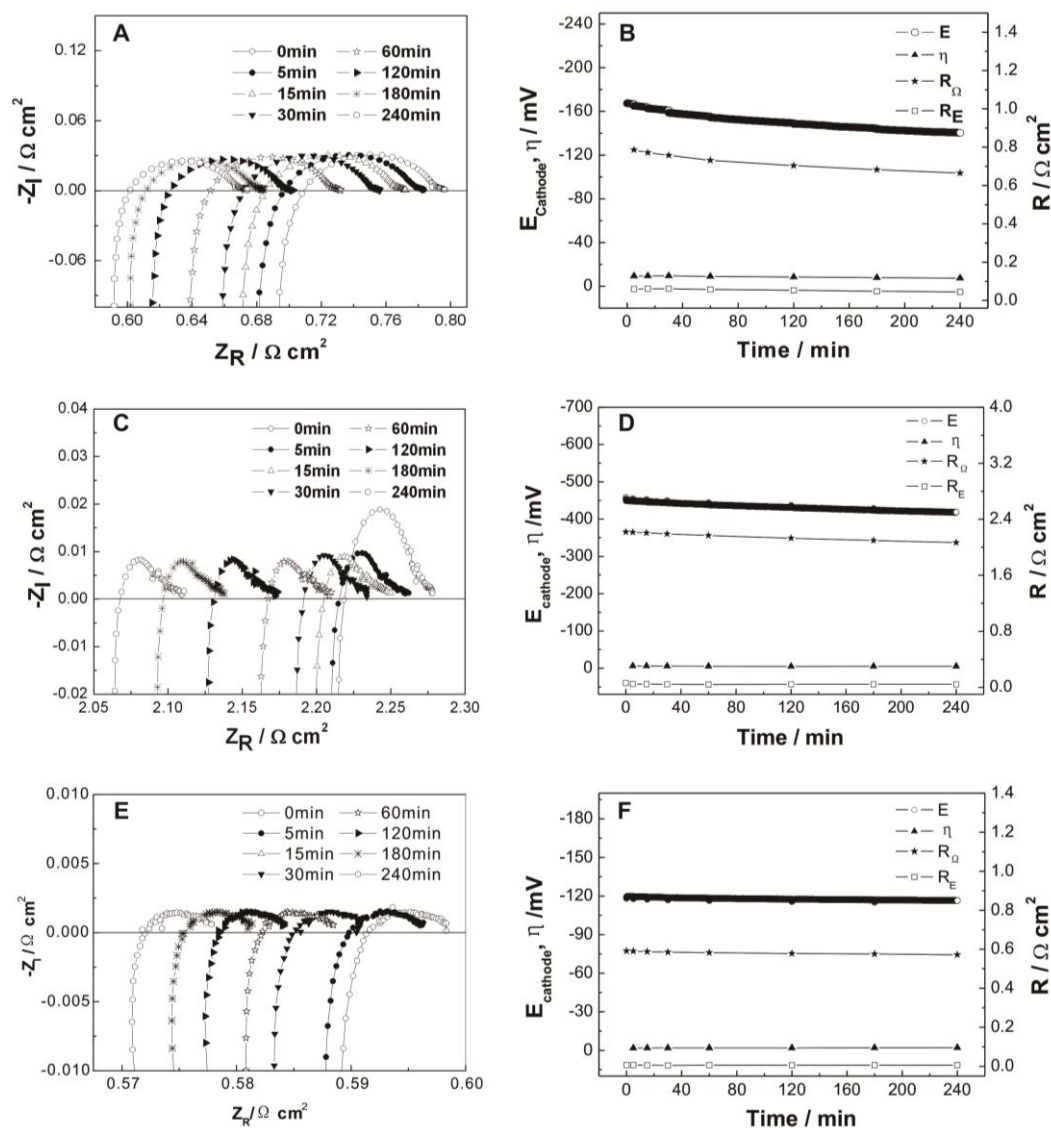
Figure S1. Nyquist plots and polarization curves of LSCF, BCFN and LSBCFN electrodes measured at 900ºC under a current passage of 200mA cm^{-2} in the absence of a Fe-Cr metallic interconnect: (A&B) LSCF, (C&D) BCFN, and (E&F) LSBCFN.
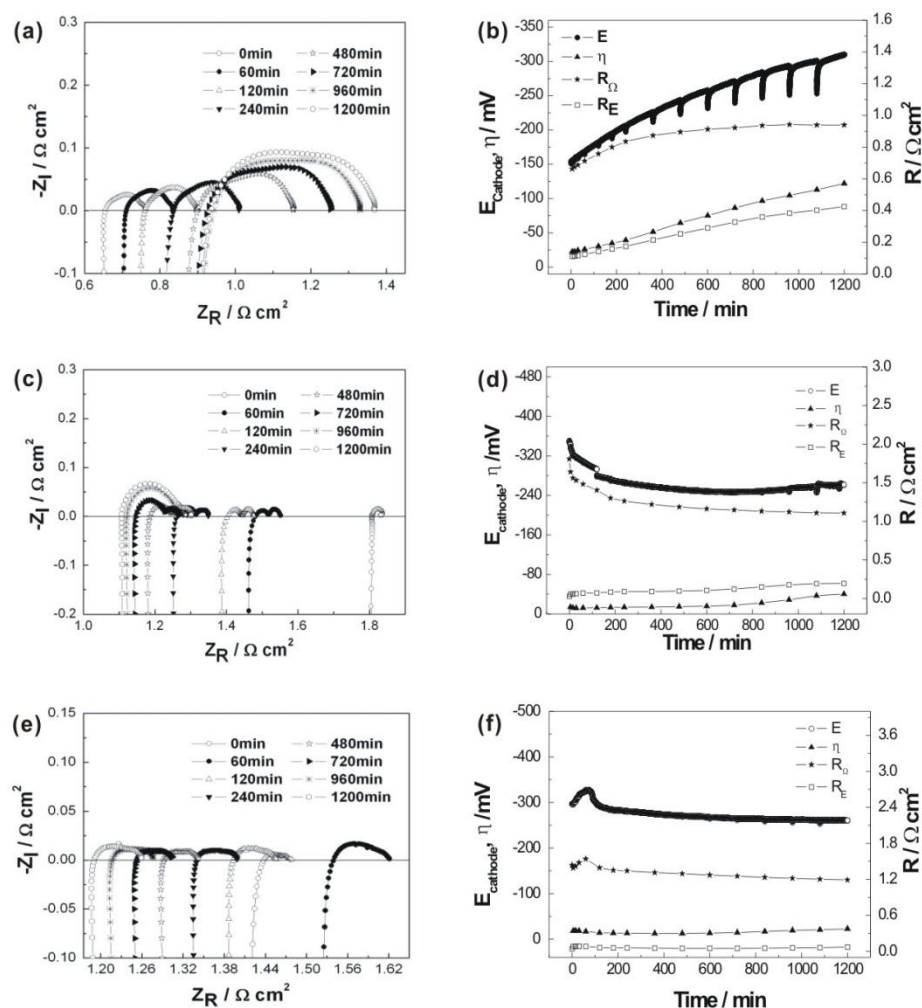
Figure S2. Impedance and polarization curves of the LSCF, BCFN and LSBCFN cathodes as a function of cathodic current passage time at 200 mAcm^{-2} and 900°C in the presence of the Fe-Cr metallic interconnect: (a,b) LSCF, (c,d) BCFN, and (e,f) LSBCFN. Impedance curves were measured at the open circuit condition.

Fig.S2 is the impedance and polarization curves of the LSCF, BCFN, and LSBCFN cathodes of the LSCF, BCFN and LSBCFN cathodes as a function of cathodic current passage time at 200 mAcm^{-2} and 900°C in the presence of the Fe-Cr metallic interconnect. Impedance curves were measured under the open circuit condition. In the presence of Fe-Cr interconnect (Figure S2 a, c, & d), some fluctuations happened in R_Ω, which can be attributed to the formation of the chromium oxides on the interconnect surface. In contrast to the nearly constant R_E and η values in the absence of the interconnect, R_E and η measured in the presence of interconnect increase with the cathodic polarization time, clearly indicating the chromium poisoning effects of the Fe-Cr metallic interconnect on the electrochemical activity of the

cathodes. For the LSCF cathode, R_E increased from 0.11 Ω cm^2 to 0.42 Ω cm^2 and η increased from 23 mV to 122 mV during the 1200 min current passage. In the case of the BCFN cathode, R_E increased from 0.14 Ω cm^2 to 0.19 Ω cm^2 while η increased from 14 mV to 40 mV at the end of the test. In the case of LSBCFN cathode, R_E increased from 0.04 Ω cm^2 to 0.07 Ω cm^2 while η increased from 18 mV to 22 mV, which are much smaller than that observed on LSCF and BCFN electrodes.

As shown previously[2], the increase in η and R_E in the presence of the metallic interconnect can be taken as an effective criterion to evaluate the chromium poisoning effects. Larger increase in η and R_E means more serious chromium poisoning effects caused by the chromium depositions at the cathodes. The increase in η for LSCF, BCFN, and LBSCFN cathodes are 99, 26, and 4 mV respectively under the current passage of 200 mA cm^{-2} while the increase in R_E for the cathode are 0.31, 0.16, and 0.03 Ω cm^2. The increase in η and R_E for the O_2 reduction in the presence of the Fe-Cr metallic interconnect on LSBCFN cathode is negligible, indicating that the LSBCFN40 cathodes has high chromium-tolerance towards Cr poisoning, as compared with the LSCF and BCFN cathodes.

To clarify the relationship between the amount of Cr deposits and the surface segregation of Sr and Ba, a semi-quantitative analysis based on the EDS result was performed. Table 1 gives the concentrations of different elements in atom % according to the EDS results of Fig.8. Table 1 has been added to the Supporting Information of the revised paper. Each value is the average of EDS spectra obtained at two neighbouring spots on the electrode surface. In comparison with the electrode in the absence of Cr depositions, there is significant change in the surface composition of the electrode in the presence of Cr depositions due to the Cr coverage and surface segregation. Here we use the content of Fe as a reference for the normalization of the total content of Sr and Ba, which has been shown to have significant effect on the Cr deposition. In the table, $R_{(Sr+Ba)/Fe}$ ratio is defined according to the equation below:

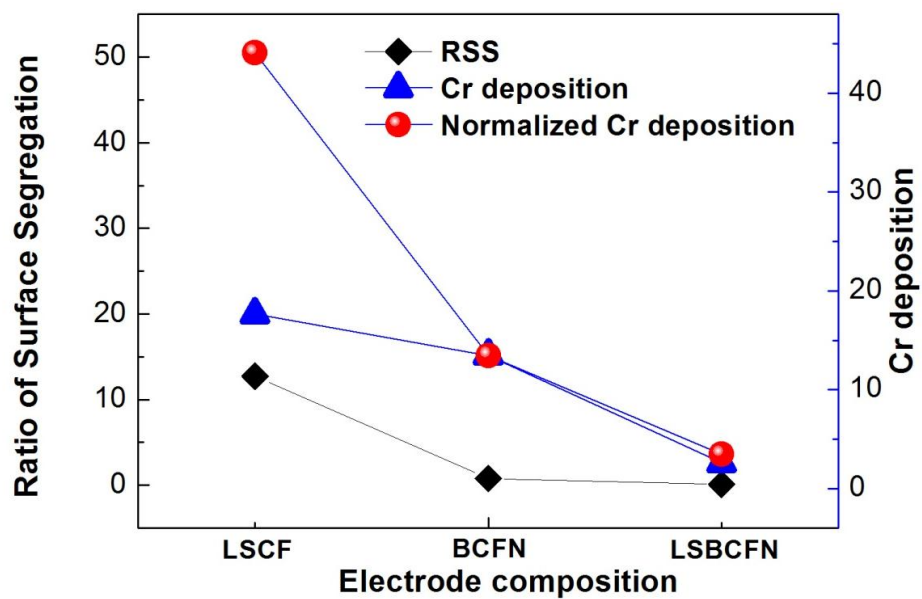$$R_{(Sr+Ba)/Fe} = C_{(Sr+Ba)} / C_{Fe} \qquad (1)$$

where $C_{(Sr+Ba)}$ is the total content of Sr and Ba, and C_{Fe} is the content of Fe according to the EDS results. The ratio of surface segregation (RSS) is defined according to the equation below:

$$RSS= [R_{(Sr+Ba)/Fe} (electrode+Cr) - R_{(Sr+Ba)/Fe} (electrode)] / R_{(Sr+Ba)/Fe} (electrode) \qquad (2)$$

where $R_{(Sr+Ba)/Fe}$ (electrode+Cr) denotes $R_{(Sr+Ba)/Fe}$ in the presence of Cr depositions and $R_{(Sr+Ba)/Fe}$ (electrode) corresponds to $R_{(Sr+Ba)/Fe}$ for the pure electrode in the absence of Cr. RSS means the increase in the percentage of the total surface content of Sr and Ba and can be used as an indication of Sr and Ba surface segregation due to the presence of Cr deposition. The figure below shows the values of C_{Cr}, and RSS of electrodes studied. The relationship between the surface segregation and Cr deposition is reasonable considering the semi-qualitative nature of the analysis. The results indicate that the Cr deposition at the electrode is closely related to the surface segregation of Sr and Ba, consistent with the previous results.

Table 1. Concentration (atom%) of elements on the electrode surface in the absence and presence of Cr deposition based on the EDS analysis.

Electrode	C_{La}	C_{Sr}	C_{Ba}	C_{Co}	C_{Fe}	C_{Nb}	C_{Cr}	$Cr_{norm.}$	$R_{(Sr+Ba)/Fe}$	RSS
LSCF	11.76	7.84	---	3.88	13.73	---	---	---	0.57	---
LSCF+Cr	2.26	18.51	---	1.22	2.36	---	17.65	44.12	7.84	12.75
BCFN	---	---	17.01	9.68	2.76	2.20	---	---	6.16	---
BCFN+Cr		---	16.78	5.17	1.52	0.66	13.47	13.47	11.04	0.79
LSBCFN	4.56	3.60	10.93	8.42	7.75	1.02	---	---	1.87	---
LSBCFN+Cr	4.20	2.94	10.81	7.36	6.60	1.02	2.62	3.45	2.08	0.11

References

1. S. P. Jiang, *Solid State Ionics*, 2002, **146**, 1-22.

2. X. B. Chen, L. Zhang, E. J. Liu and S. P. Jiang, *Int. J. Hydrog. Energy*, 2011, **36**, 805-821.