## **Electronic Supplementary Information**

## Boost Steam-Tolerance and Electrochemical Performance of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-6</sub>-based Air Electrode for Protonic Ceramic Electrochemical Cells

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Figure S1. ECR responses of the LSCF and PCO-LSCF bars measured at 750-650 °C.



**Figure S2.** EIS of the PCFC single cells with LSCF (a) and PCO-LSCF (b) electrodes at 550-650 °C using  $H_2$  (3%  $H_2O$ ) as the fuel and humidified air (3%  $H_2O$ ) as the oxidant under OCV.



**Figure S3.** EIS of the PCEC single cells with LSCF (a) and PCO-LSCF (b) electrodes at 550-650 °C using  $H_2$  (3%  $H_2$ O) as the fuel and humidified air (30%  $H_2$ O) as the steam source under OCV.



**Figure S4.** (a) I-V curves measured in PCEC mode at 600 °C with various  $H_2O$  concentrations (3-30%) in the air electrode; (b) EIS recorded in PCEC mode at 600 °C with various  $H_2O$  concentrations (3-30%) in the air electrode.

**Note for Figure S4:** The change of  $H_2O$  partial pressure has little effect on the electrochemical performance of single cells, which is consistent with the results reported by Duan *et al.*<sup>1</sup> and He *et al.*<sup>2</sup> Additionally, the results of Zhou *et al.*<sup>3</sup> for the change of  $R_p$  value under different steam concentrations were consistent with this work.



Figure S5. SEM image of symmetric cell supported by BZCYYb electrolyte.



Figure S6. EIS of LSCF symmetric cell in the air containing various  $H_2O$  concentrations (3-30%) at 650 °C.



**Figure S7.** DRT analysis of LSCF air electrode based on the EIS at 650 °C under various  $H_2O$  concentrations (3-30%).



Figure S8. XRD patterns of the LSCF (a) and PCO-LSCF (b) powder after being exposed to humidified air (50%  $H_2O$ ) at 750 °C for 72 h.



**Figure S9.** (a) Durability test of a PCEC single cell with a LSCF electrode at 600 °C (3%  $H_2O$ , *J*=-0.5 A cm<sup>-2</sup>); (b) EIS recorded at different times during the durability test.



Figure S10. SEM images of LSCF air electrode before (a) and after (b) the 60-hour's durability test under the conditions of 600  $^{\circ}$ C and 3% H<sub>2</sub>O.

Materials	D <sub>chem</sub> (cm <sup>2</sup> s <sup>-1</sup> )	k <sub>chem</sub> (cm s <sup>-1</sup> )	T (°C)	Ref.
$PrBaCo_2O_{5+\delta}$	-	3.90×10 <sup>-4</sup>	750	4
$Bi_{0.5}Sr_{0.5}Fe_{0.95}Nd_{0.05}O_{3\cdot\delta}$	0.46×10 <sup>-5</sup>	1.48×10 <sup>-5</sup>	700	5
$SrFe_{0.9}Nb_{0.1}O_{3\text{-}\delta}$	-	2.20×10 <sup>-4</sup>	700	6
$Pr_{1.2}Sr_{0.8}NiO_{4+\delta}$	-	4.40×10 <sup>-4</sup>	750	7
$Sr_2Fe_{1.5}Mo_{0.5-x}In_xO_{6-\delta}$	4.20×10 <sup>-5</sup>	4.98×10 <sup>-4</sup>	800	8
$Ba_{0.5}Sr_{0.5}FeO_{3\text{-}\delta}$	-	2.0×10 <sup>-4</sup>	700	9
PCO-LSCF	4.40×10 <sup>-5</sup>	4.40×10 <sup>-4</sup>	700	This work
	5.44×10 <sup>-5</sup>	5.74×10 <sup>-4</sup>	750	This work

**Table S1.** Comparison of  $k_{chem}$  and  $D_{chem}$  values between PCO-LSCF and other air electrode materials.

**Table S2.** Current density of single cells with LSCF air electrode at 550-650 °C and 1.1-1.3 V.

т (%с)	Current Density	Current Density	Current Density
1 ( C)	@1.3 V (A cm <sup>-2</sup> )	@1.2 V (A cm <sup>-2</sup> )	@1.1 V (A cm <sup>-2</sup> )
650	1.85	0.924	0.331
600	1.14	0.444	0.123
550	0.550	0.185	0.041

**Table S3.** Current density of single cells with PCO-LSCF air electrode at 550-650 °C and 1.1-1.3 V.

T (%C)	Current Density	Current Density	Current Density
1 ( C)	@1.3 V (A cm <sup>-2</sup> )	@1.2 V (A cm <sup>-2</sup> )	@1.1 V (A cm <sup>-2</sup> )
650	2.04	0.998	0.360
600	1.22	0.483	0.139
550	0.585	0.221	0.049

## References

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