Supporting Information

Investigation of Real Polarization Resistance for Electrode Performance in Proton-Conducting Electrolysis Cells

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Working mechanism of a PCEC

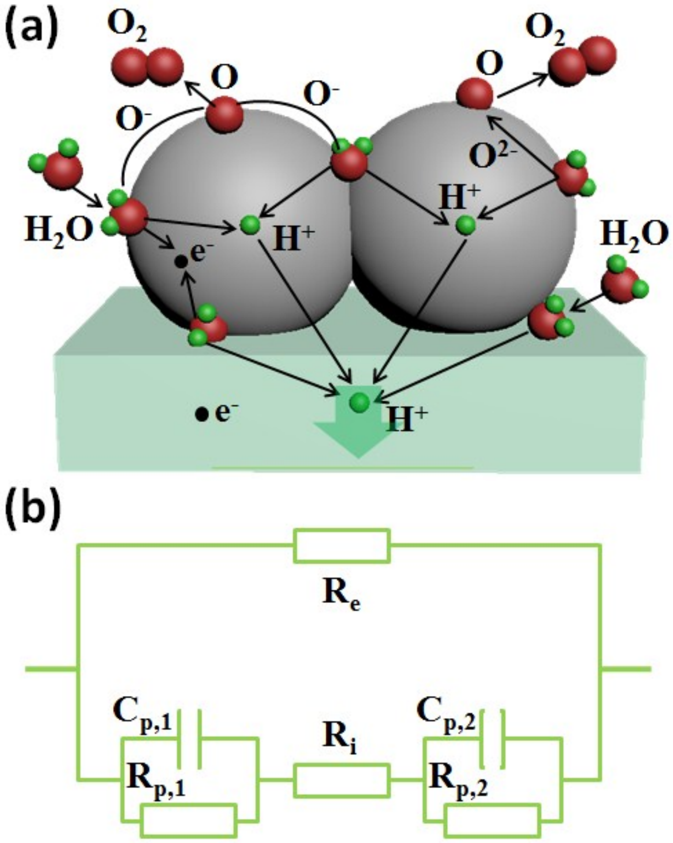

Figure S1. (a) The working mechanism of single phase air electrode with simultaneous proton, oxygen andelectron conduction for PCECs. (b) Simplified equivalent circuit of a solid-state cell based onan electrolyte of MIECs.

Electrical conductivity of SLF samples

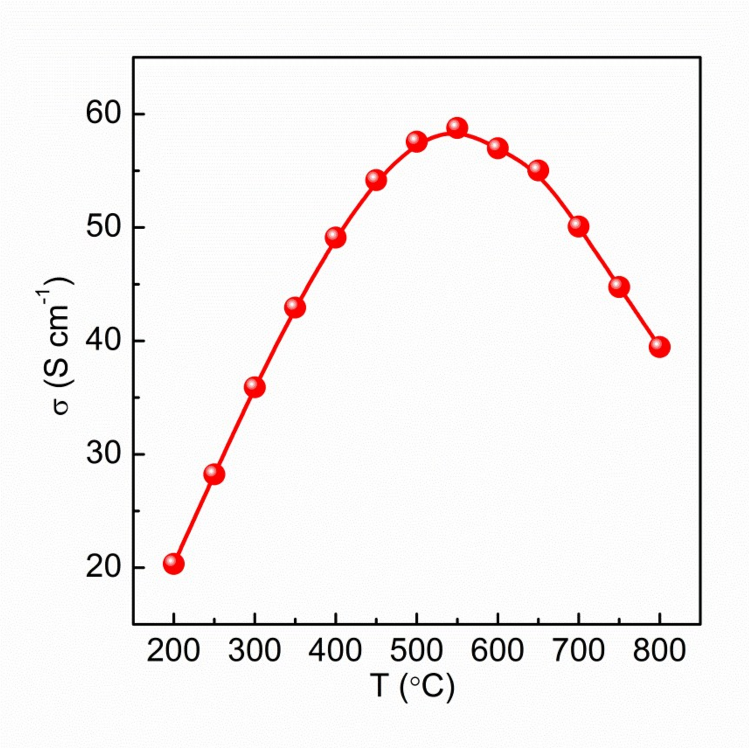

Figure S2. Electrical conductivities of SLF measured at various temperatures.

Figure S2 shows the total conductivity of SLF at various temperatures. The conductivities of SLF are 57.6, 58.8, 57.0 55.0 and 50.1 Scm^{-1} at 500, 550, 600, 650 and 700 °C, respectively. The conductivity increases first with the temperature increasing and then decreases, achieves the highest valve of 58.8 Scm^{-1} at 550°C. The undoped $Sr_3Fe_2O_7$ achieves the maximum conductivity of 60 Scm^{-1} at 500°C with the same relationship of conductivity with temperature. This doping concentration of La in $Sr_3Fe_2O_7$ has little negative effect on the conducting property because of the higher oxidation of La^{3+} than Sr^{2+} lead to less oxygen vacancy. (S1, S2)

Electrochemical impedance spectra (EIS) of button cells

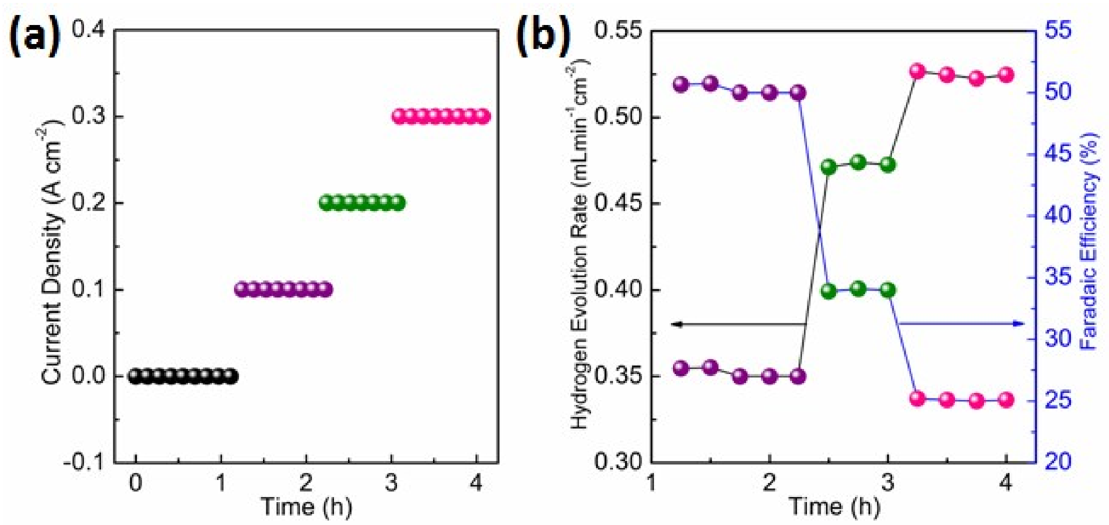

Figure S3. (a) Short-term stability test at various electrolysis current densities and (b) the correspoding hydrogen evolution rate and Faradaic efficiency at 700 °C.

Faradaic efficiency has been determined with 30 % H_2-N_2 and 20 % H_2O-air injected into cathode and anode, respectively. After the electrolysis current achieve stable for 1 h, the actual hydrogen evolution rates can be measured, which are 0.351, 0.473 and 0.525 ml min^{-1} cm^{-2} at 100, 200 and 300 mA cm^{-2}, respectively. When the Faradaic efficiency is 100 %, hydrogen evolution rates can be theoretically calculated as 0.70, 1.39 and 2.09 ml min^{-1} cm^{-2} at 100, 200 and 300 mA cm^{-2}, respectively. And therefore, the actual Faradaic efficiencies of electrolysis during the stability test can be estimated as 50.2 , 34.0 and 25.1 % at current densities of 0.1, 0.2 and 0.3 Acm^{-2}. (S3)

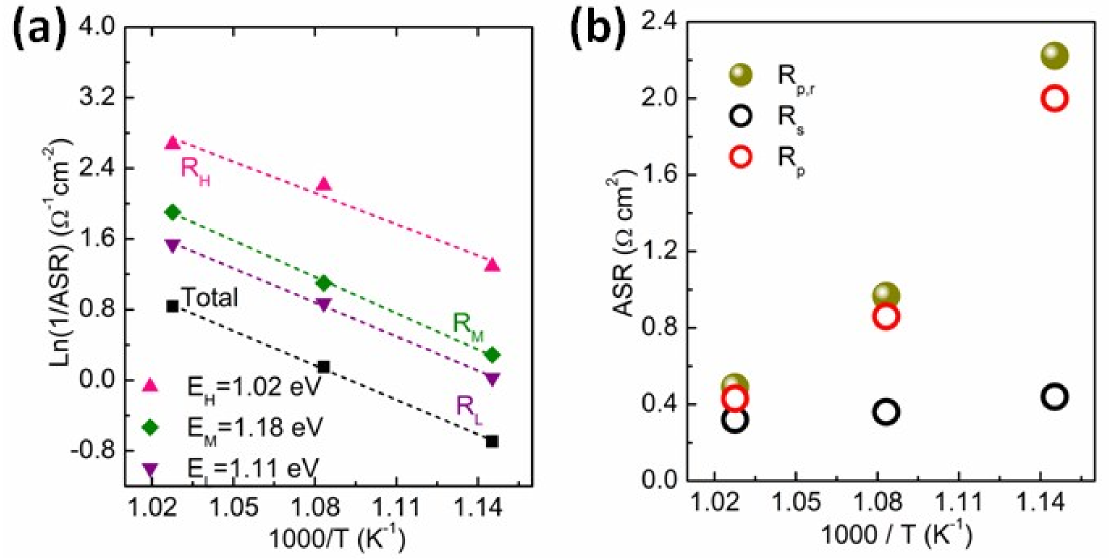

Figure S4. (a) Temperature dependence of apparent polarization resistances: R_H, R_M, R_L and R_p (Total, $R_H+R_M+R_L$). (b) R_s, R_p and $R_{p,r}$ for PCEC single cell using the SLF air electrode measured under OCV condition.

Table S1. The values for each sub-step of R_H, R_M, and R_L and ratios of $R_i/R_{i,r}$ (i=H, M, L) at various temperatures under OCV condition humid H_2/ 20% H_2O-air atmosphere.

Temperature (°C)	R_H (Ωcm^2)	$R_H/R_{H,r}$	R_M (Ωcm^2)	$R_M/R_{M,r}$	R_L (Ωcm^2)	$R_H/R_{L,r}$	R_p (Ωcm^2)
700	0.069	0.846	0.149	0.873	0.215	0.892	0.433
650	0.110	0.853	0.333	0.887	0.418	0.903	0.861
600	0.275	0.866	0.751	0.900	0.975	0.910	2.001

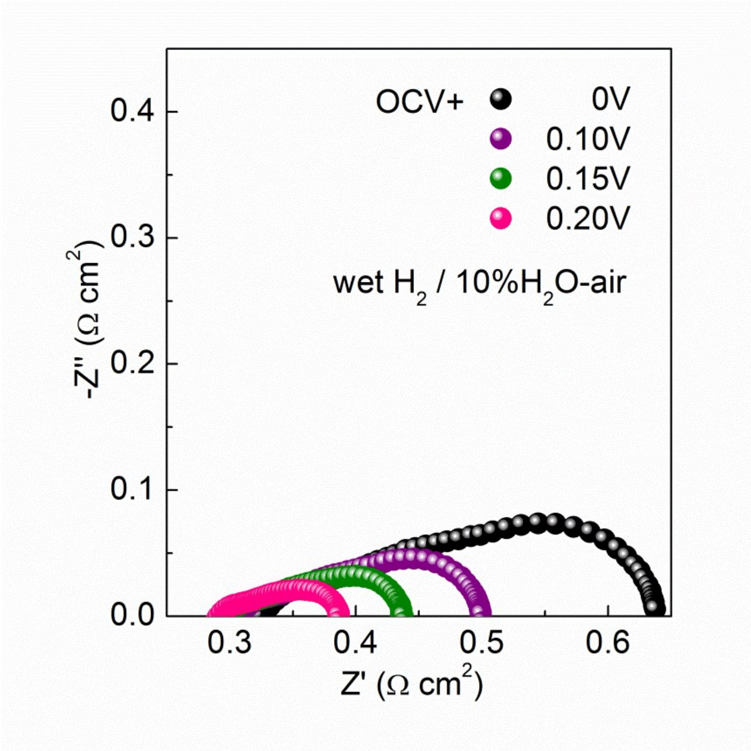

Figure S5. EIS of the PCEC single cell using the SLF air electrode measured at various electrolysis voltages (OCV+ 0.00V, 0.10V, 0.15V, 0.20V) in humid H_2/ 10% H_2O-air atmosphere at 700 °C.

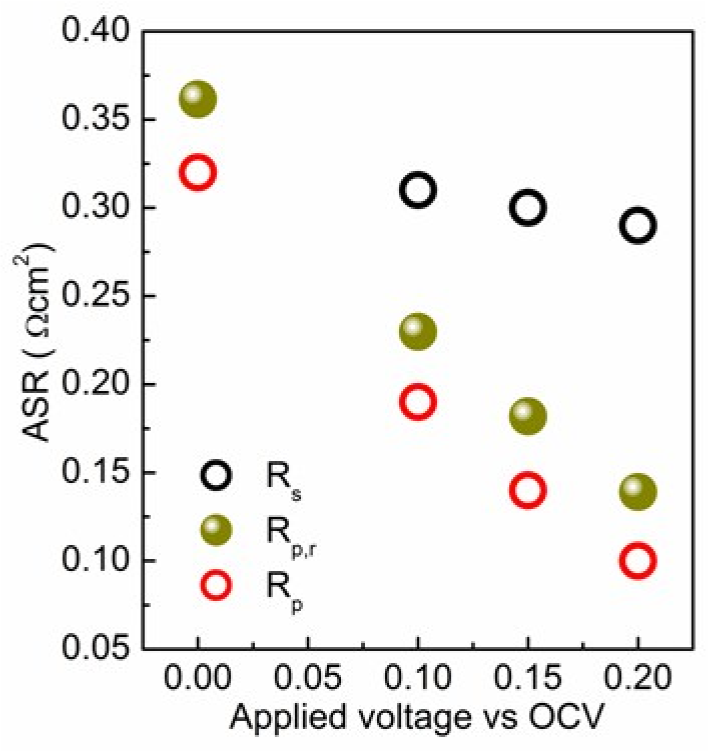

Figure S6. (a) R_s, R_p and $R_{p,r}$ for a PCEC using the SLF anode.

Table S2. Values of R_H, R_M, and R_L under various electrolysis voltage in humid H_2/ 10% H_2O-air atmosphere.

Applied voltage *vs* OCV (V)	R_H (Ωcm^2)	R_M (Ωcm^2)	R_L (Ωcm^2)	R_p (Ωcm^2)
0.00	0.064	0.116	0.138	0.318
0.10	0.036	0.079	0.076	0.191
0.15	0.030	0.063	0.048	0.141
0.20	0.023	0.047	0.026	0.096

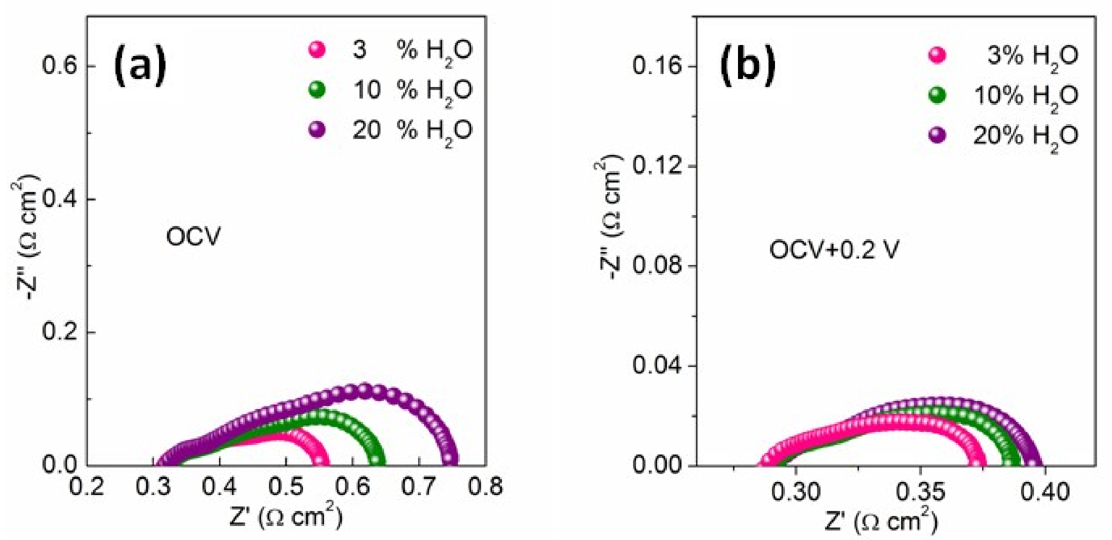

Figure S7. EIS of the PCEC single cell using the SLF air electrode measured in various pH_2O under (a) OCV and (b) OCV +0.20 V condition in wet H_2/ 10% H_2O-air atmosphere at 700 °C.

Table S3. Values of R_H, R_M and R_L in various pH_2O under OCV and OCV+0.20 V modes.

	pH_2O (atm)	R_H (Ωcm^2)	R_M (Ωcm^2)	R_L (Ωcm^2)	R_p (Ωcm^2)
OCV	0.03	0.046	0.098	0.094	0.238
	0.10	0.064	0.116	0.138	0.318
	0.20	0.069	0.149	0.215	0.433
OCV+0.2V	0.03	0.022	0.044	0.020	0.086
	0.10	0.023	0.047	0.026	0.096
	0.20	0.025	0.051	0.029	0.105

Reference

S1. Z. Wang, W. Yang, S. P. Shafi, L. Bi, Z. Wang, R. Peng, C. Xia, W. Liu and Y. Lu, *J. Mater. Chem. A,* 2015, **3**, 8405-8412.

S2. D. Huan, Z. Wang, Z. Wang, R. Peng, C. Xia and Y. Lu, *ACS Appl. Mater. Interfaces,* 2016, **8**, 4592−4599.

S3. S. M. Babiniec, R. Sandrine and N. P. Sullivan, *Int. J. Hydrogen Energy*, 2015, **40**, 9278-9286.