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Supplementary information

Barium carbonate as synergistic catalyst for H_2O/CO_2 reduction reaction at Ni-yttria stabilized zirconia cathode of solid oxide electrolysis cell

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Supplementary figures

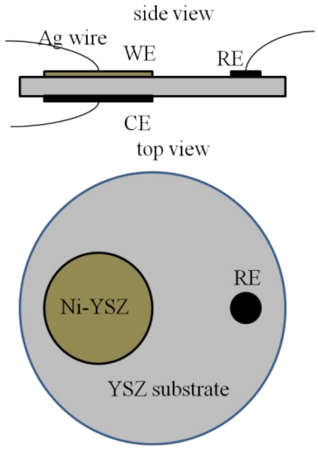

Fig. S1. The schematic of the three-electrode construction where Ni-YSZ is the working electrode (WE) while the counter electrode (CE) and reference electrode (RE) are platinum.

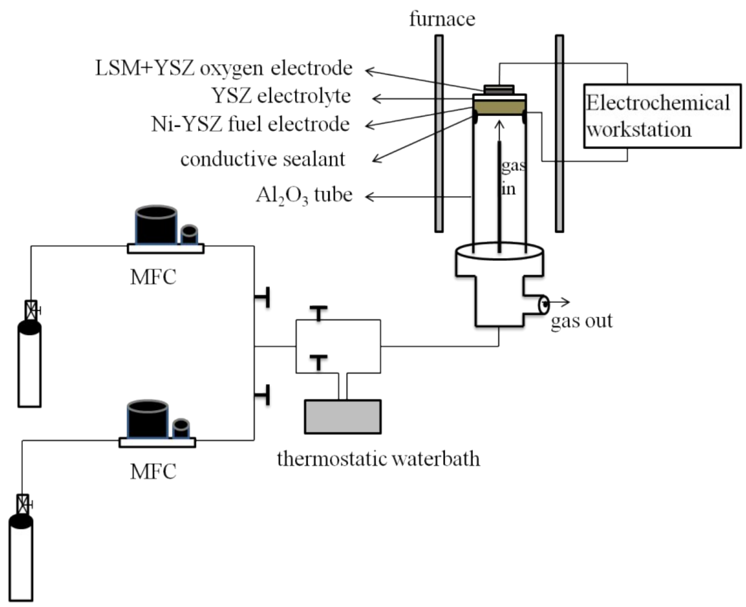

Fig. S2 The schematic illustration for single cell tests.

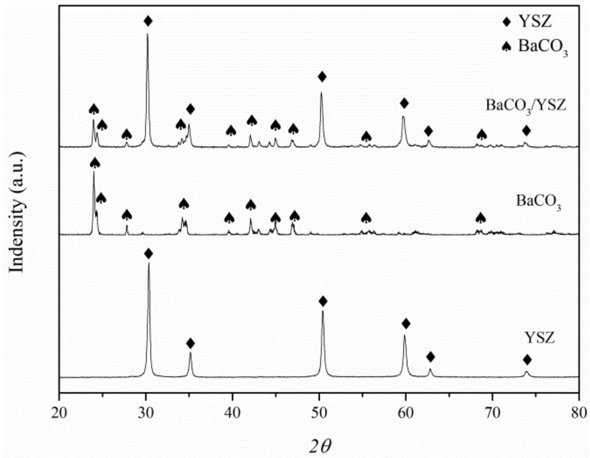

Fig. S3 The XRD patterns of YSZ powder, $BaCO_3$ powder, made by heating $Ba(Ac)_2$ at 800 °C for 1 hour, and $BaCO_3$ infiltrated YSZ powder, made by dropping $Ba(Ac)_2$ solution (0.6 mol L^{-1}) into YSZ powder followed by heating at 800 °C for 1 hour. The $BaCO_3$ content is 34.8 wt.%.

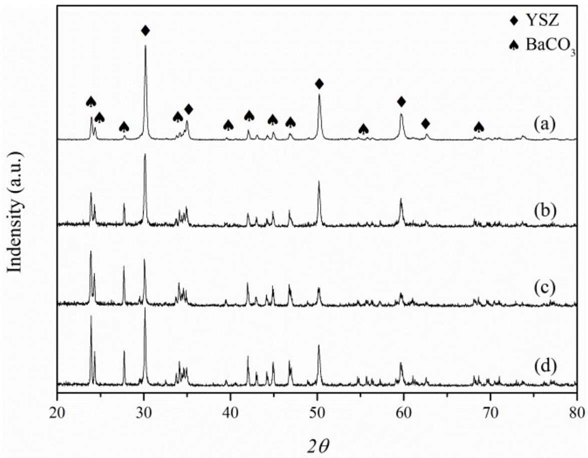

Fig. S4 The XRD patterns of $BaCO_3$ infiltrated YSZ (a) before exposing to SOEC operating atmosphere, (b) after exposing to 20%H_2O-80%H_2 atmosphere at 800 °C for 20 hours, (c) after exposing to 70%CO_2-30%CO atmosphere at 800 °C for 20 hours, and (d) after exposing to 20%H_2O-10%H_2-49%CO_2-21%CO atmosphere at 800 °C for 20 hours.

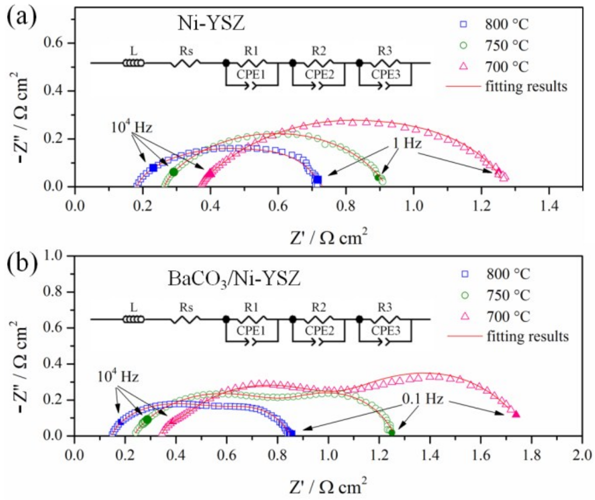

Fig. S5 Impedance spectra measured under open circuit conditions for the single cell (a) Ni-YSZ and (b) $BaCO_3$ infiltrated Ni-YSZ fuel electrode, respectively, when ambient air is used as the oxidant and humidified hydrogen as the fuel. The data was obtained after the single cell was tested in fuel cell model for 90 minutes with a constant current density of 0.5 A cm^{-2} at 800 °C and for additional 5 minutes to measure the I-V curves as shown in Fig. 3.

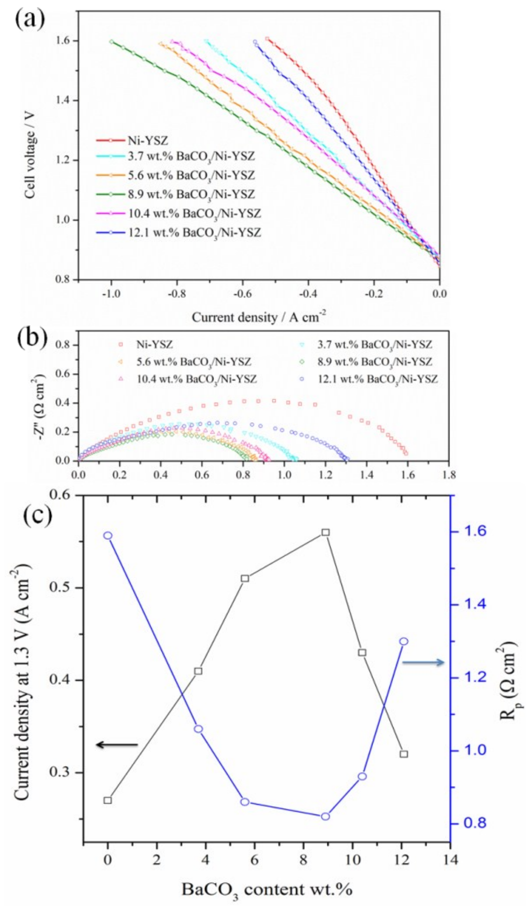

Fig. S6 The single cell performance at 800 °C for electrolysis of CO_2 using 70%CO_2-30%CO as the fuel with different $BaCO_3$ contents. (a) I-V curves, (b) AC impedance spectra measured under open-circuit conditions and the resistance corresponding to the electrolyte and lead wires is deducted to clearly compare the electrode performance and (c) the current density at 1.3 V and the interficial polarization resistance under open-circuit conditions as a function of $BaCO_3$ content.

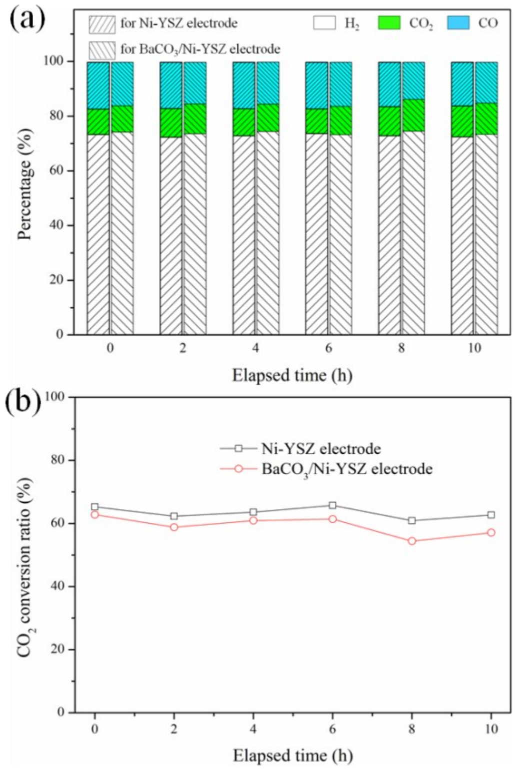

Fig. S7 (a) Out gas percentage and (b) the CO_2 conversion ratio as a functional of elapsed time under SOEC condition with a current density of -0.5 A cm^{-2} for Ni-YSZ electrode and 8.9 wt.% $BaCO_3$/Ni-YSZ electrode when 80%H_2-20%CO_2 is used as the fuel with a gas flow of 20 mL min^{-1}.

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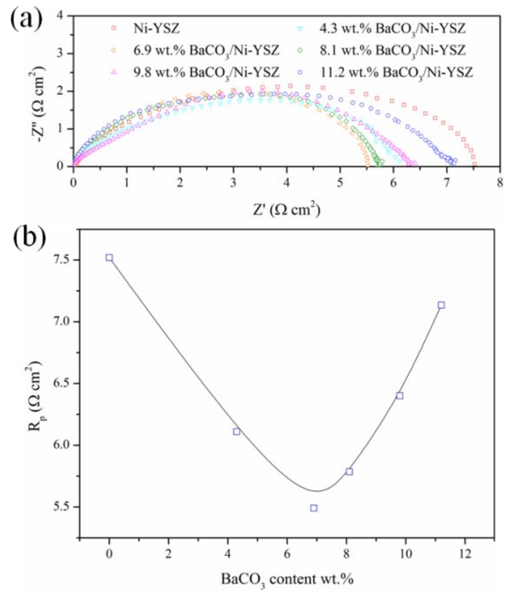

Fig. S8 (a) Impedance spectra measured at 800 °C for CO_2 electrolysis in 70%CO_2-30%CO atmosphere on Ni-YSZ cathodes with different $BaCO_3$ contents using three-electrode installation at a bias of -0.3 V, where the resistance corresponding to the electrolyte and lead wires is deducted, (b) interfacial polarization resistance as a function of $BaCO_3$ content.

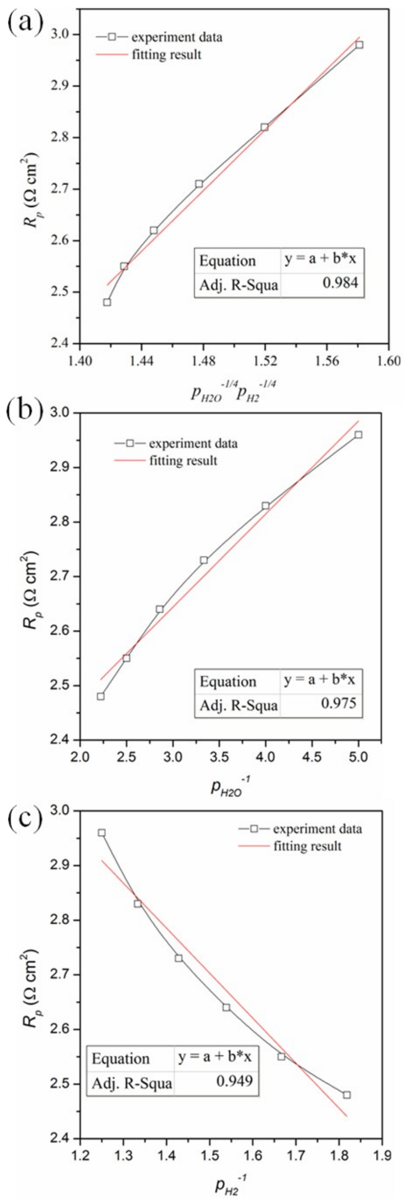

Fig. S9 Polarization resistance as a function of partial pressure as listed in Table 2 to figure out the rate-determining step for H_2O electrolysis. The resistance is obtained using three-electrode installation at a bias of -0.3 V in series of H_2O contents with H_2 as the carrier gas.

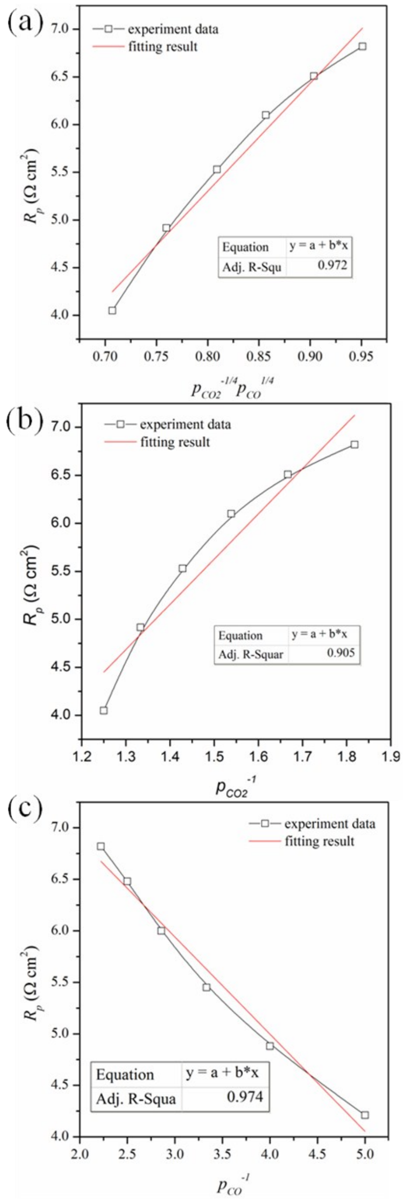

Fig. S10 Polarization resistance as a function of partial pressure as listed in Table 2 to figure out the rate-determining step for CO_2 electrolysis. The resistance is obtained using three-electrode installation at a bias of -0.3 V in series of CO_2 contents with CO as the carrier gas.

Supplementary table

Table S1 The fitting polarization resistance under open circuit conditions before and after $BaCO_3$ infiltration from Fig. S5.

T(°C)	Ni-YSZ			$BaCO_3$/Ni-YSZ		
	R1 ($\Omega\cdot cm^2$)	R2 ($\Omega\cdot cm^2$)	R3 ($\Omega\cdot cm^2$)	R1 ($\Omega\cdot cm^2$)	R2 ($\Omega\cdot cm^2$)	R3 ($\Omega\cdot cm^2$)
800	0.047	0.434	0.052	0.054	0.523	0.132
750	0.091	0.481	0.072	0.117	0.662	0.231
700	0.177	0.585	0.131	0.197	0.710	0.487

Table S2 Out gas percentage and CO_2 conversion ratio under open circuit condition (RWGS only) and under a constant current of -0.5 A cm^{-2} (RWGS+SOEC) with a flow of 20 mL min^{-1} and 80%H_2-20%CO_2 as the fuel for Ni-YSZ/YSZ/LSM+YSZ cell and 8.9 wt.%$BaCO_3$/ Ni-YSZ/YSZ/LSM+YSZ cell.

Cell configuration	Elapsed time (h)	Operate condition	Outlet gas component (%)			CO_2 conversion ratio (%)
			H_2	CO_2	CO	
Ni-YSZ/ YSZ/ LSM+YSZ	0	RWGS	71.56	13.54	14.90	52.4
		RWGS+SOEC	73.29	9.28	17.43	65.3
	2	RWGS	71.99	14.28	13.73	49.0
		RWGS+SOEC	72.32	10.43	17.25	62.3
	4	RWGS	71.73	13.94	15.40	52.3
		RWGS+SOEC	72.8	9.89	17.31	63.6
	6	RWGS	69.28	13.38	15.34	53.4
		RWGS+SOEC	73.62	9.04	17.34	65.7
	8	RWGS	71.74	14.11	14.05	49.9
		RWGS+SOEC	72.81	10.64	16.55	60.9
	10	RWGS	72.09	14.77	13.14	47.1
		RWGS+SOEC	72.43	11.28	16.29	62.7
$BaCO_3$/ Ni-YSZ/ YSZ/ LSM+YSZ	0	RWGS	72.54	14.98	12.48	45.4
		RWGS+SOEC	74.18	9.61	16.21	62.8
	2	RWGS	71.29	15.23	13.48	47
		RWGS+SOEC	73.54	10.89	15.57	58.8
	4	RWGS	72.39	14.08	13.53	49.0
		RWGS+SOEC	74.39	10.01	15.60	60.9
	6	RWGS	71.17	14.86	13.97	48.1
		RWGS+SOEC	73.24	10.32	16.44	61.4
	8	RWGS	73.24	14.38	12.38	46.3
		RWGS+SOE	74.49	11.63	13.88	54.4

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	10	RWGS	72.96	14.79	12.25	45.3
		RWGS+SOEC	73.37	11.43	15.20	57.1