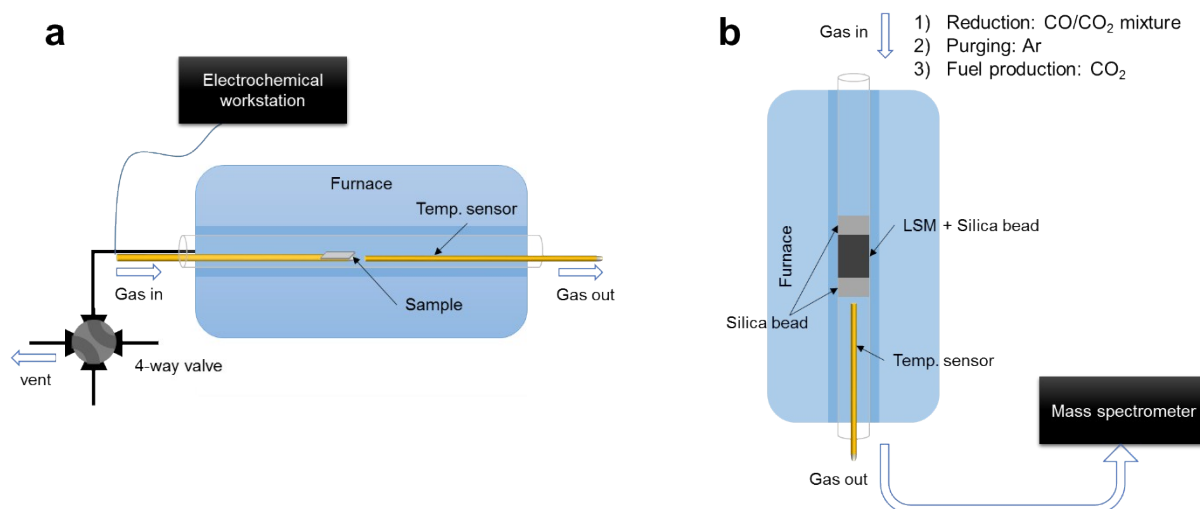
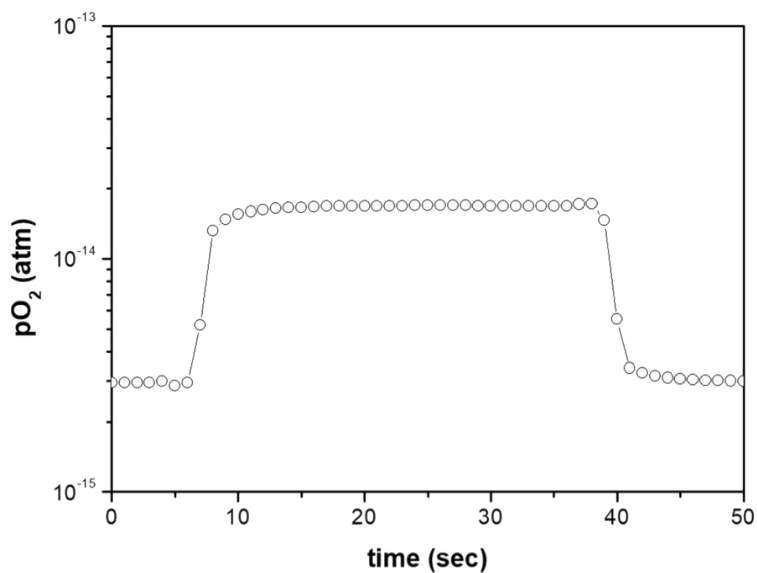


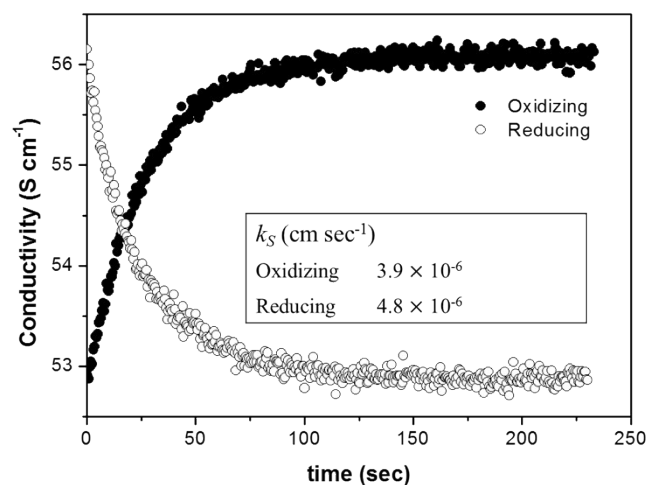
### Electronic Supplementary Information (ESI)



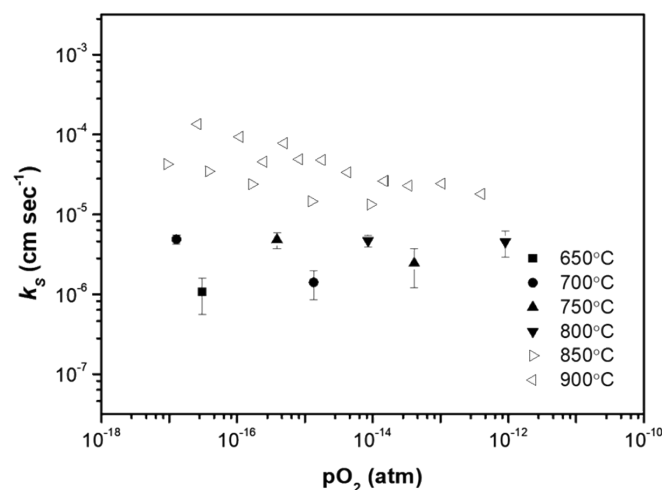
**Figure S1.** Schematic diagrams of (a) the electrical conductivity relaxation process and (b) the isothermal reactor.



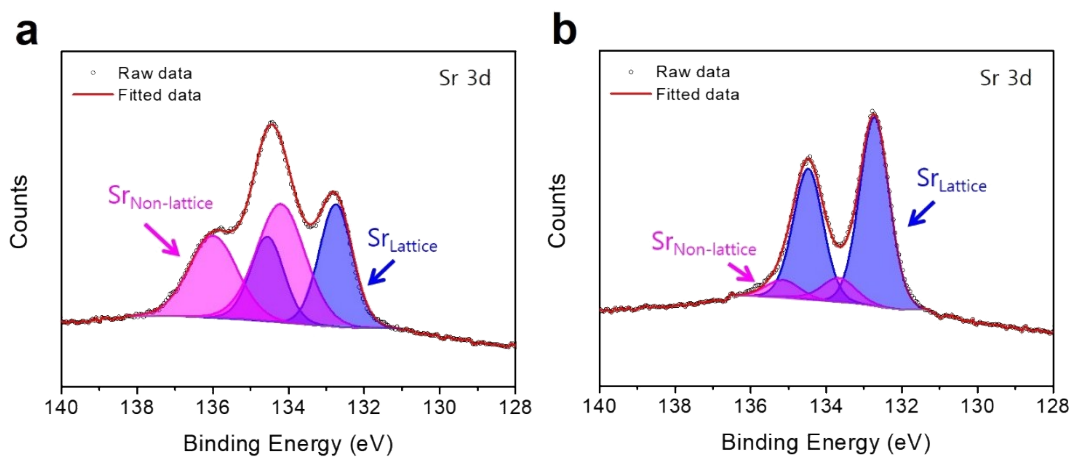
**Figure S2.** Oxygen partial pressure change upon a sudden change in the gas mixture flowing into the reactor; the gas was switched within 5 seconds, much faster than the electrical conductivity relaxation time.



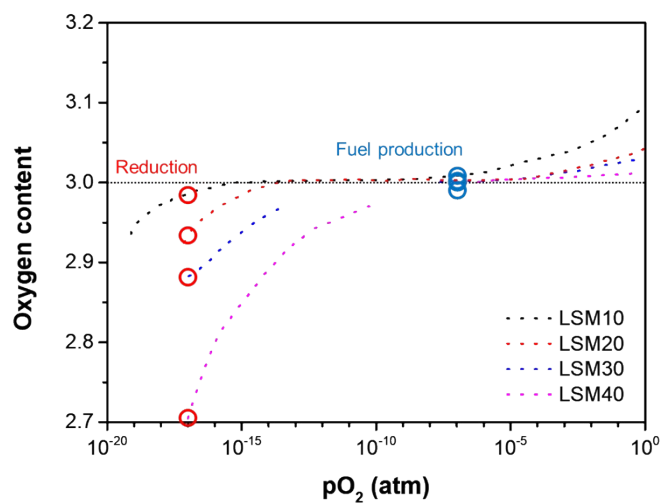
**Figure S3.** Raw conductivity relaxation profiles of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  ( $x = 0.2$ ) along reducing and oxidizing directions for a  $p\text{O}_2$  switch between  $2.9 \times 10^{-15}$  atm and  $1.5 \times 10^{-14}$  atm at  $800^\circ\text{C}$  using  $\text{CO}/\text{CO}_2$ . The relaxation profiles are almost identical, indicating that the  $p\text{O}_2$  change is small enough to ensure that  $k_S$  values are identical along both directions and that the system response is linear.



**Figure S4.** Comparison of the  $k_S$  values of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  ( $x = 0.2$ ) in the literature (opened) and in this study (closed).<sup>20</sup> The values here are in agreement with those in the literature.



**Figure S5.** Sr 3d spectra of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  ( $x = 0.2$ ) films (a) before and (b) after the removal of the outmost layers by chemical etching after the electrical conductivity relaxation measurements.



**Figure S6.** Oxygen content in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3, 0.4$ ) at  $800^\circ\text{C}$ . During the feasibility test of fuel production, cycling was performed between  $p\text{O}_2$  levels of  $1.0 \times 10^{-17}$  atm ( $\text{CO}/\text{CO}_2$  mixture) and  $1.0 \times 10^{-7}$  atm ( $\text{CO}_2$ ). Reproduced from Ref. 9 with permission from The Royal Society of Chemistry.

(mol/mol LSM)

Sr content	Powder			Films		
	La	Sr	Mn	La	Sr	Mn
0.1	0.77	0.11	1.12	0.83	0.10	1.07
0.2	0.69	0.19	1.12	0.73	0.20	1.07
0.3	0.60	0.29	1.11	0.68	0.29	1.03
0.4	0.51	0.39	1.10	0.57	0.39	1.04

**Table S1.** Inductively coupled plasma mass spectrometry (ICP-MS) composition analysis of the metal elements in the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  powders and films.

Sr content	Before/After chemical etching		
	La	Sr	Mn
0.1	60.12/41.14	8.60/5.09	31.28/53.77
0.2	46.89/37.13	16.38/10.20	36.70/52.64
0.3	34.87/34.30	18.43/12.19	46.66/53.48
0.4	39.26/30.97	17.71/16.18	43.00/52.85

**Table S2.** Chemical composition of the surface of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  films before and after chemical etching as analyzed by X-ray photoelectron spectroscopy (XPS).