Remarkable chemical adsorption of manganese-doped titanate for direct carbon dioxide electrolysis

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Part 1 Supporting Materials for direct CO_2 electrolysis

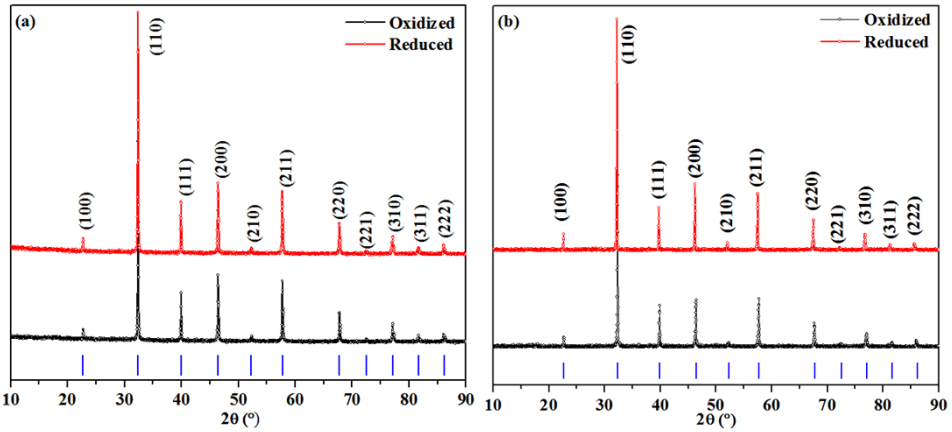

Fig.S1(a) XRD patterns of oxidized and reduced $La_{0.2}Sr_{0.8}TiO_{3+\delta}$ (LSTO) powders; (b) XRD patterns of oxidized and reduced $La_{0.2}Sr_{0.8}Ti_{0.9}Mn_{0.1}O_{3+\delta}$ (LSTMO) powders.

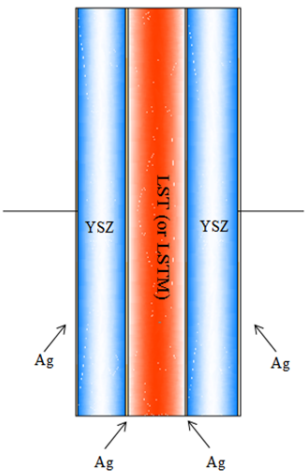

Fig.S2 System configuration of testing samples for two terminal blocking electrode methods (a) Ag/YSZ/Ag/LSTO/Ag/YSZ/Ag or Ag/YSZ/Ag/LSTO/Ag/YSZ/Ag

The electron-blocking electrode method has been widely used for ionic conductivity test [1-9]. In the system, the electron flux is blocked by YSZ layer because YSZ is

considered to be almost a pure oxygen ion conductor. Glass seal was used to prevent oxygen leakage along the sides of the assembled samples. Applying a DC voltage on the outside of both samples and YSZ layers, a stable current can be observed at designated temperature. The transformation of oxygen and oxide ion is repeated several times in the testing system. Then the total resistance caused by double layer materials can be calculated. Therefore, the ionic conductivity of sample (σ_{ion}) can be worked out by its oxygen ionic resistance.

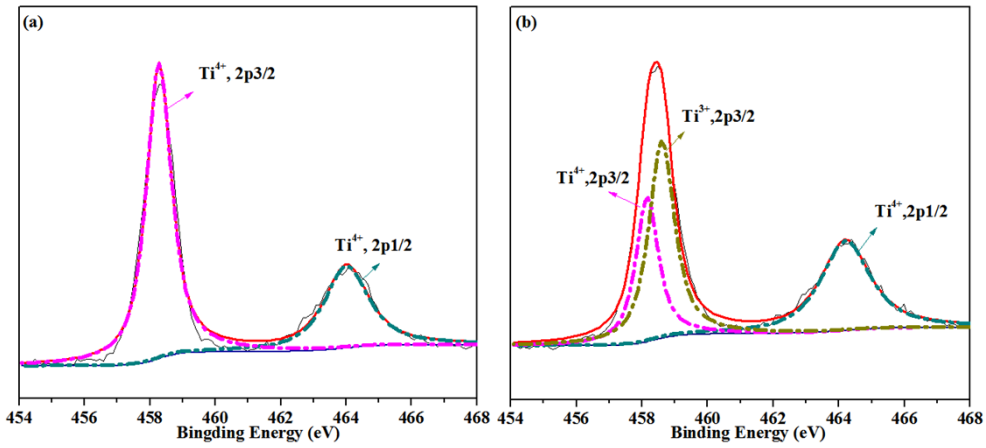

Fig.S3 XPS results for Ti in (a) oxidized and (b) reduced $La_{0.2}Sr_{0.8}TiO_{3+\delta}$ (LSTO).

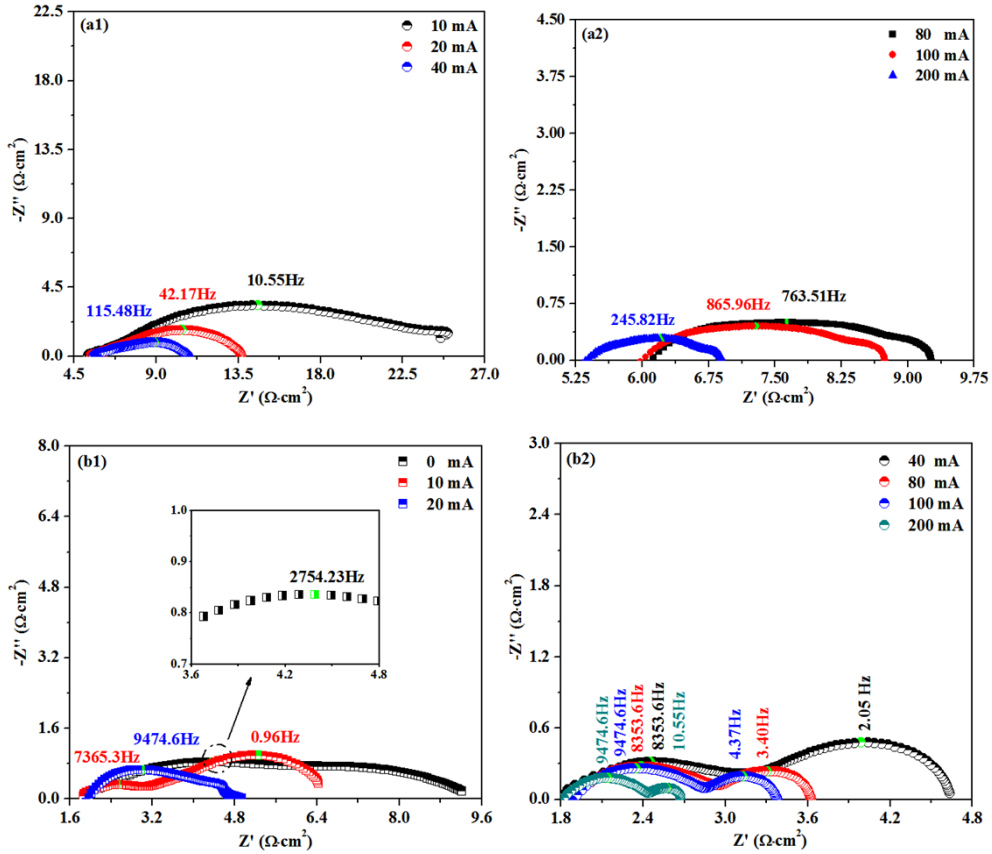

Fig.S4 AC impedance of symmetric cells tested in CO_2 under different applying currents with a configuration of (a1) (a2) LSTO-SDC/YSZ/LSTO-SDC and (b1) (b2) LSTMO-SDC/YSZ/LSTMO-SDC

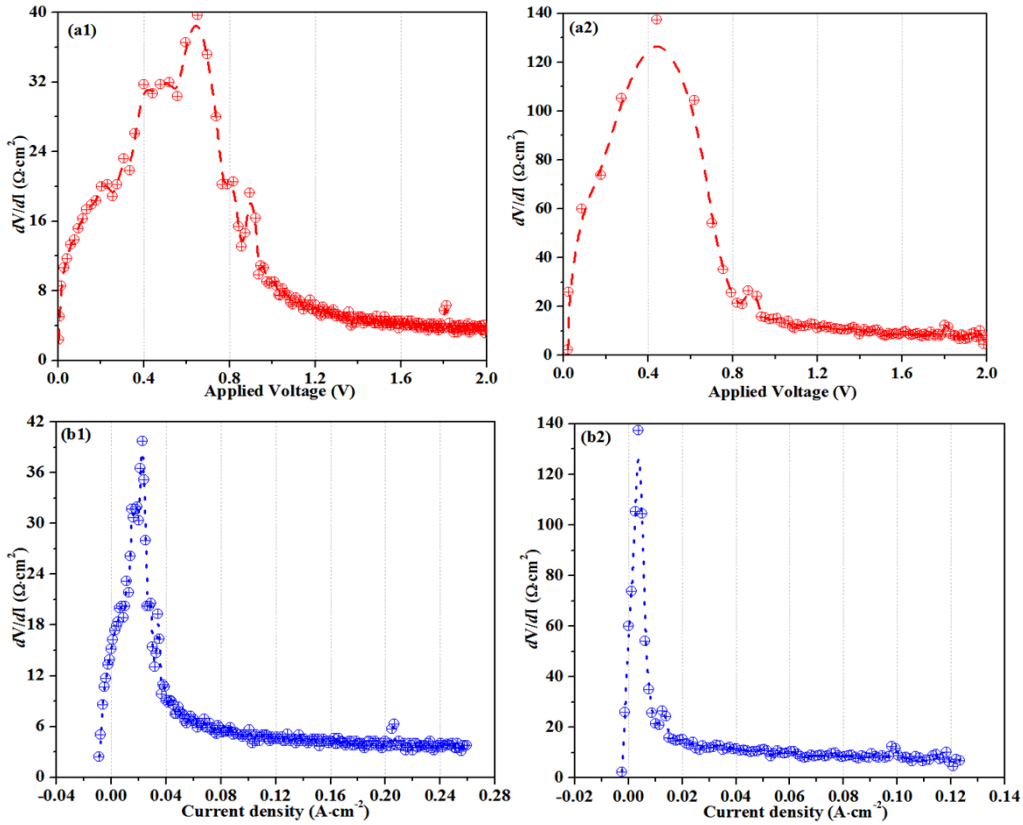

Fig.S5 The *d*V/*d*I was plotted versus current density andapplied voltage where the data were from the I-V curve of the SOEs based on (a1) (b1) LSTMO-SDC and (a2) (b2) LSTO-SDC electrode for direct CO_2 electrolysis at 800 ºC.

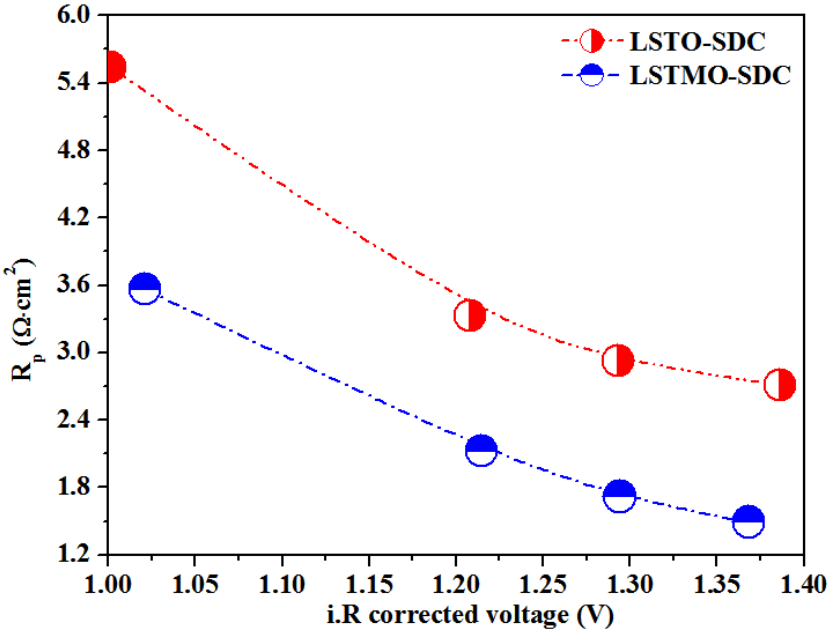

Fig.S6 R_p versus i.R corrected voltage during the CO_2 electrolysis at 800 ºC.

Part 2 SOEs based on LSTMO-SDC and LSTO-SDC for steam electrolysis

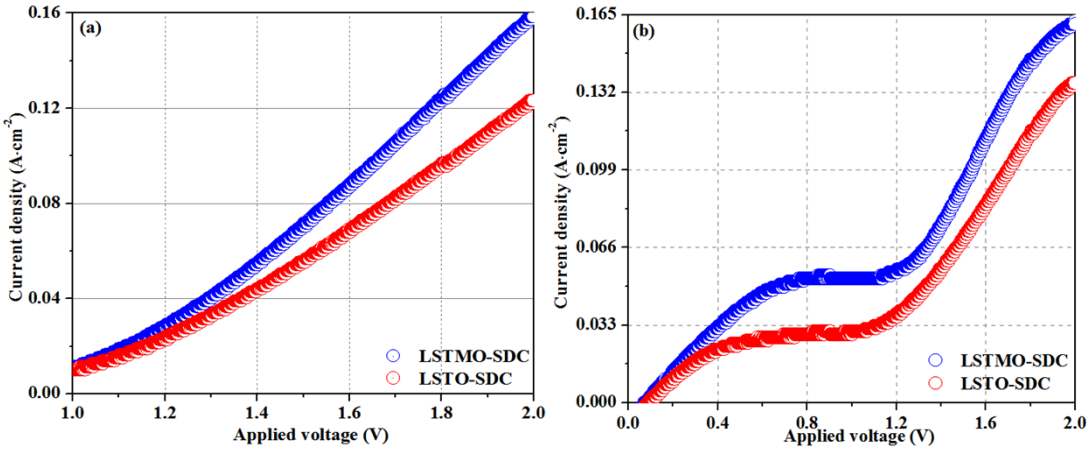

Fig.S7 I-V curves of SOEs with cathodes based on LSTO-SDC and LSTMO-SDC for steam electrolysis in (a) 3% H_2O/5% H_2/92% Ar and (b) 3% H_2O/97% Ar.

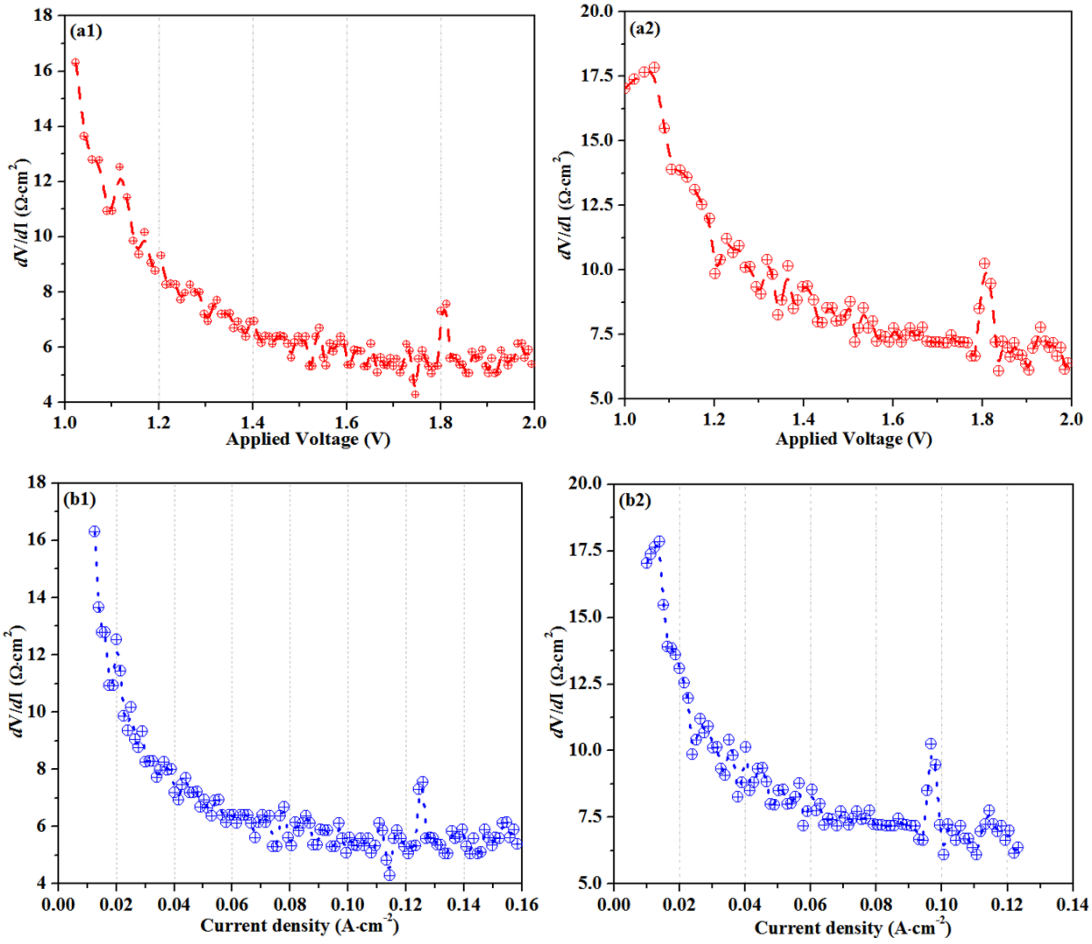

Fig.S8 The dV/dI was plotted versus current density and applied voltage where the data were from the I-V curves of the SOEs based on (a1) (b1) LSTMO-SDC and (a2) (b2) LSTO-SDC electrode at 800 ºC in 3% H_2O/5% H_2/92% Ar.

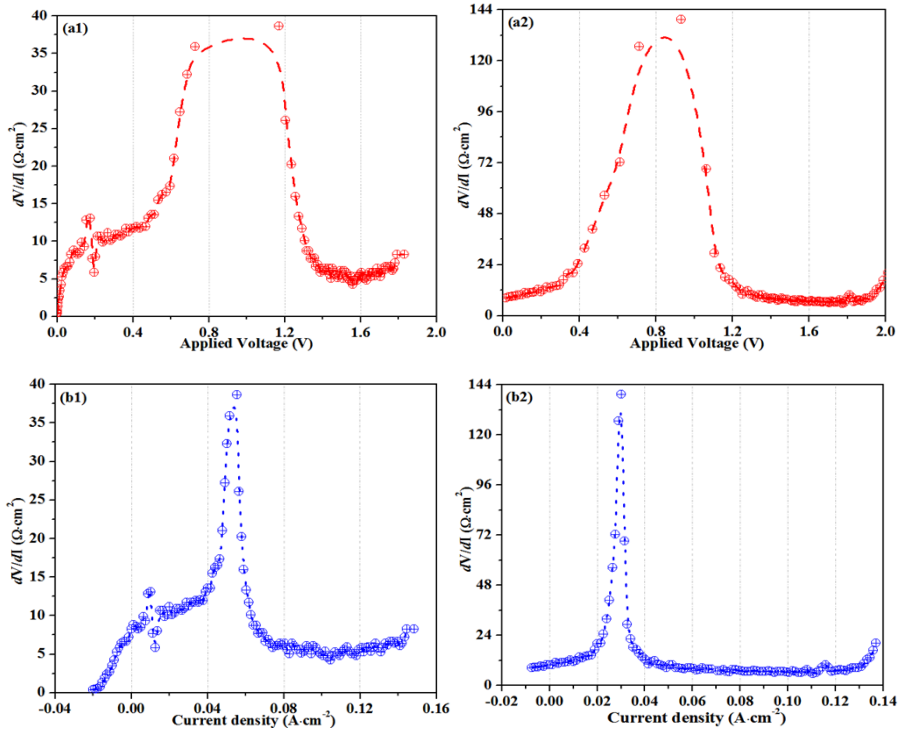

Fig.S9 The *d*V/*d*I was plotted versus current density andapplied voltage where the data were from the I-V curves of the SOEs based on (a1) (b1) LSTMO-SDC and (a2) (b2) LSTO-SDC electrode at 800 ºC in 3% H_2O/97% Ar.

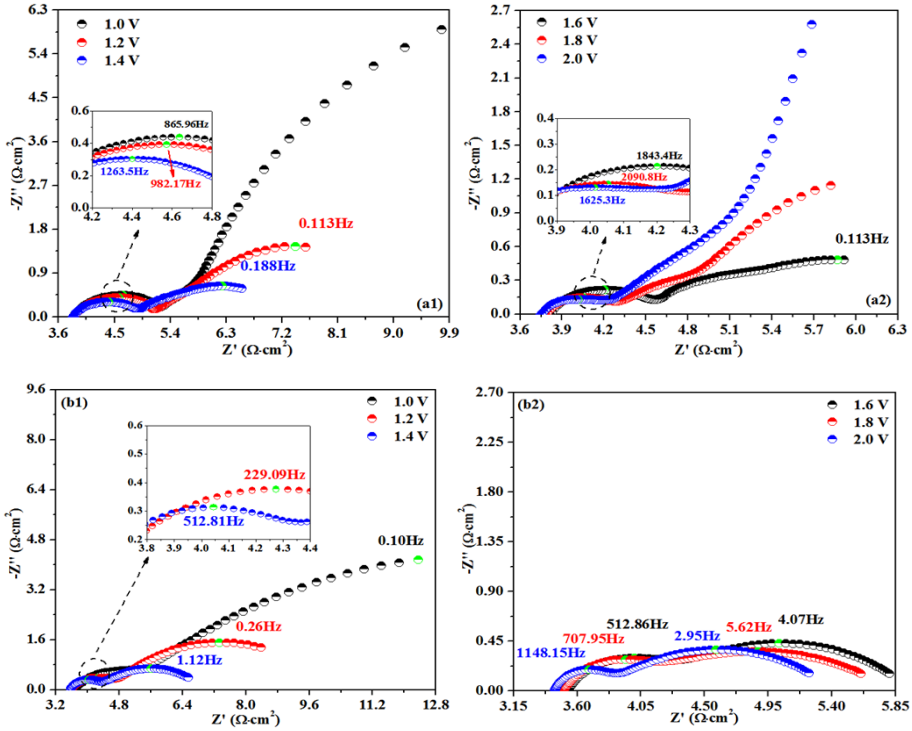

Fig.S10 AC impedance of single SOEs with cathodes based on (a1) (a2) $La_{0.2}Sr_{0.8}TiO_{3+\delta}$-$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (LSTO-SDC) and (b1) (b2) $La_{0.2}Sr_{0.8}Ti_{0.9}Mn_{0.1}$-$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (LSTMO-SDC) under different applied potentials at 800 ºC in 3% H_2O/5% H_2/92% Ar.

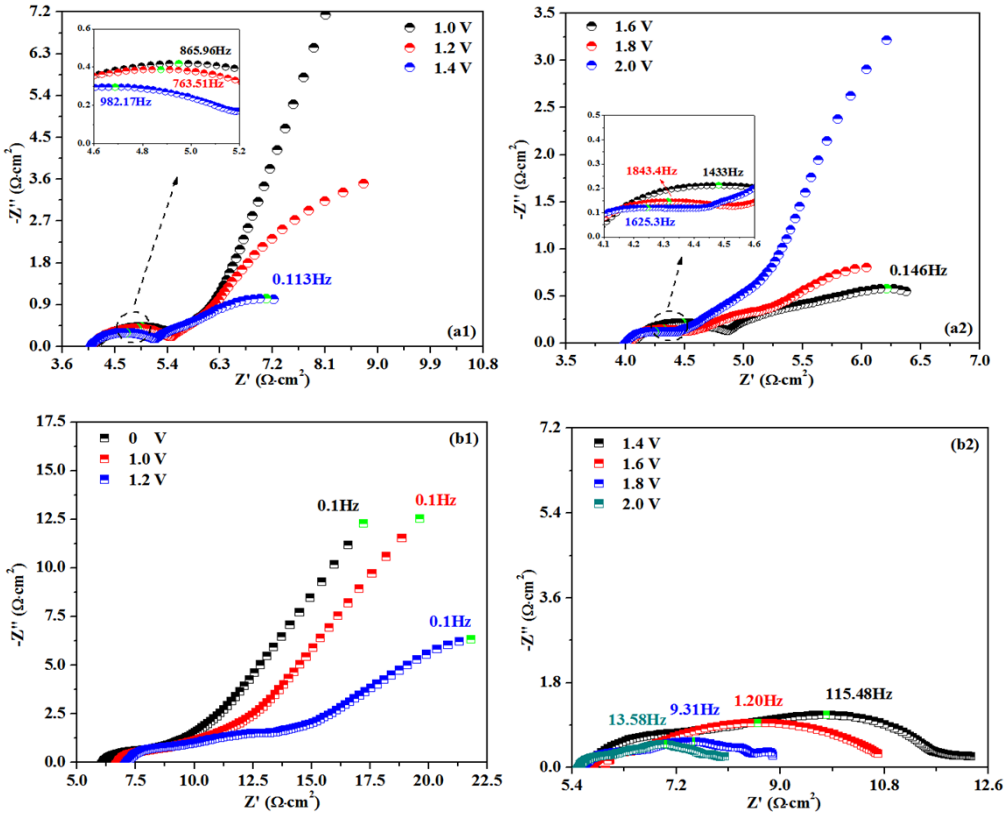

Fig.S11 AC impedance of single SOEs with cathodes based on (a1) LSTO-SDC and (a2) LSTMO-SDC under different applied potentials at 800 ºC in 3% H_2O/97% Ar.

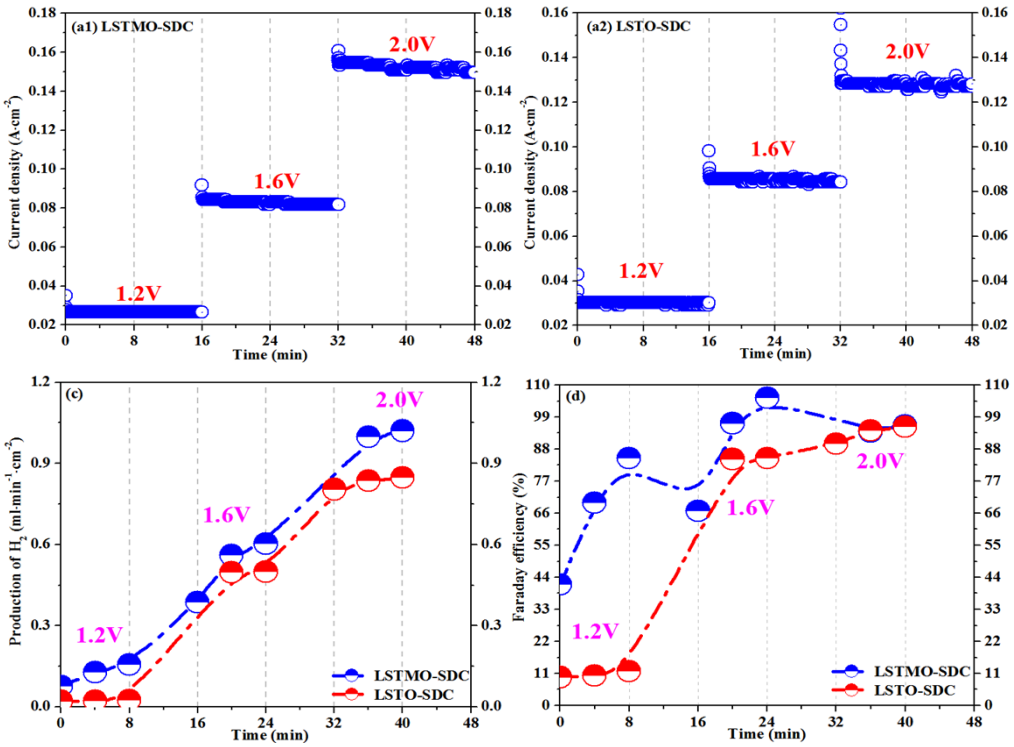

Fig.S12 (a1) (a2) Short-term performance of steam electrolysis with 5% H_2/3% H_2O/92% Ar; (b) The production of H_2 during the electrolysis and (c) its corresponding Faraday efficiency.

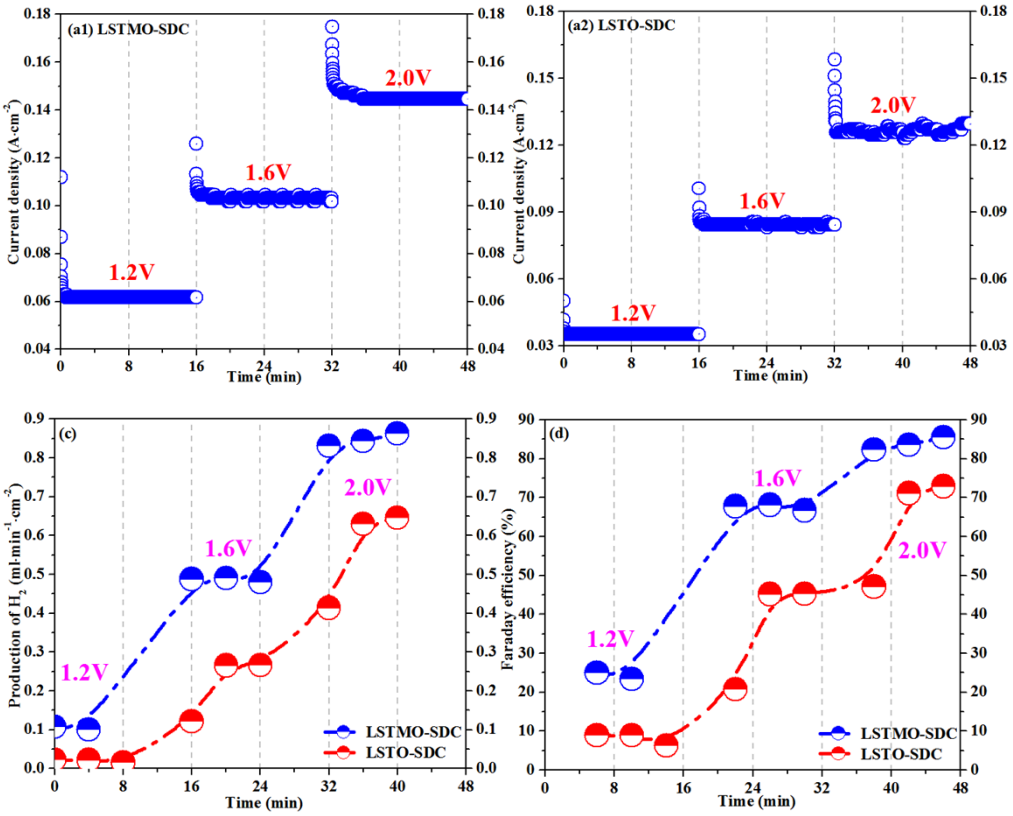

Fig.S13 (a1) (a2) Short-term performance of steam electrolysis with 3% H_2O/97% Ar;(b) The production of H_2 during the electrolysis and (c) its corresponding Faraday efficiency.

Table 1-1 Details about the steam electrolysis based on LSTMO-SDC electrode in 3%H_2O/5%H_2/97% Ar.

Applied Voltage	**Input Gas flow**	**Output Gas flow**			**Faraday Efficiency**		
(V)	**(ml·min^{-1})**	**(ml·min^{-1})**			**(%)**		
1.2	30	0.076	0.128	0.156	41.48	69.63	84.88
1.6	30	0.387	0.561	0.602	66.76	96.88	105.61
2.0	30	/	0.998	1.02	/	93.99	96.16

Table 1-2 Details about the steam electrolysis based on LSTO-SDC electrode in 3% H_2O/5% H_2/97% Ar.

Applied Voltage	**Input Gas flow**	**Output Gas flow**			**Faraday Efficiency**		
(V)	**(ml·min^{-1})**	**(ml·min^{-1})**			**(%)**		
1.2	30	0.020	0.021	0.025	9.73	10.20	11.67
1.6	30	/	0.497	0.499	/	84.55	84.91
2.0	30	0.804	0.836	0.847	89.89	94.37	95.60

Table 2-1 Details about the steam electrolysis based on LSTMO-SDC electrode in 3% H_2O/97% Ar.

Applied Voltage	**Input Gas flow**	**Output Gas flow**			**Faraday Efficiency**		
(V)	**(ml·min^{-1})**	**(ml·min^{-1})**			**(%)**		
1.2	31	0.107	0.101	/	24.98	23.44	/
1.6	31	0.488	0.490	0.480	67.79	68.12	66.73
2.0	31	0.831	0.844	0.863	82.37	83.62	85.51

Table 2-2 Details about the steam electrolysis based on LSTO-SDC electrode in 3% H_2O/97% Ar

Applied Voltage (V)	**Input Gas flow ($ml \cdot min^{-1}$)**	**Output Gas flow ($ml \cdot min^{-1}$)**			**Faraday Efficiency (%)**		
1.2	28	0.022	0.022	0.016	8.99	8.87	6.32
1.6	28	0.122	0.266	0.266	20.72	45.18	45.31
2.0	28	0.414	0.630	0.646	47.15	71.11	72.89

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