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Enhanced CO₂ electrolysis with SrTiO₃ cathode through dual doping strategy

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Abstract

The significant role of perovskite defect chemistry through A-site doping of strontium titanate with lanthanum for CO₂ electrolysis properties is demonstrated. Here we present a dual strategy of A-site deficiency and promoting adsorption/activation by making use of redox active dopants such as Mn/Cr linked to oxygen vacancies to facilitate CO₂ reduction at perovskite titanate cathode surfaces. Solid oxide electrolyzers based on oxygen-excess La_{0.2}Sr_{0.8}Ti_{0.9}Mn(Cr)_{0.1}O_{3+δ}, A-site deficient (La_{0.2}Sr_{0.8})_{0.9}Ti_{0.9}Mn(Cr)_{0.1}O_{3-δ} and undoped La_{0.2}Sr_{0.8}Ti_{1.0}O_{3+δ} cathodes are evaluated. *In situ* infrared spectroscopy reveals that the adsorbed and activated CO₂ adopts an intermediate chemical state between a carbon dioxide molecule and a carbonate ion. The double strategy leads to

optimal performance being observed after 100 h of high-temperature operation and 3 redox cycles, suggesting a promising cathode material for CO₂ electrolysis.

Introduction

Solid oxide electrolyzers (SOEs) have been attracting great interest due to their high efficiency in converting electrical energy into chemical energy¹⁻². They can exploit available heat streams such as nuclear power plants or industrial heat to maximize electrical efficiency while both thermodynamic and kinetic advantages can be expected because of the high operating temperatures³. The oxide ion-conducting SOEs can directly electrolyse carbon dioxide into carbon monoxide and pure oxygen under external applied potentials. At the cathode, the CO₂ molecules are electrochemically reduced and split into CO while the generated O²⁻ ions are transported through the electrolyte membrane to the anode compartment where the pure O₂ gas is formed and released^{2, 4}.

Such materials have formed a starting point for SOEs development and primarily include Ni/yttria-stabilized zirconia (Ni/YSZ) cermet for the cathode and (La,Sr)MnO₃ for the anode⁵. Recent studies have considered alternative materials to Ni/YSZ for the SOEs cathode, and these have included the utilization of (La,Sr)TiO_{3+δ}⁶ and La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃⁷ perovskites. A primary motivation for the investigation of alternative SOEs cathode materials is the instability of Ni/YSZ to redox cycling, which in practice requires feeding a small quantity of protecting gas such as hydrogen or CO at the electrolysis cell cathode inlet in order to avoid the formation of NiO at low or zero electrolysis current density⁸⁻⁹. In contrast, oxide perovskites, are generally stable to redox cycling and can therefore be operated without the requirement of protecting gas in the electrolysis cell cathode inlet. Furthermore, appropriate doping of the A/B-site of ABO₃ perovskites, would allow properties to be tuned specifically to meet the demands of SOEs, such as operation under high temperature and strongly reducing environment.

La-doped strontium titanates exhibit favourable chemical, dimensional, redox, thermal and mechanical stability¹⁰. In addition, these perovskites demonstrate good electronic conductivity under reducing conditions due to the formation of the $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple, which is particularly suitable for the reducing environment encountered at the electrolysis cell cathode¹¹. Lattice defect formation is made possible by aliovalent doping of the A-site of SrTiO_3 , for example, some of the divalent Sr^{2+} cations are substituted with trivalent La^{3+} cations. The defect chemistries considered here are oxygen-excess ($\text{ABO}_{3+\delta}$) and A-site deficiency ($\text{A}_{1-x}\text{BO}_3$). However, cathode performance for CO_2 electrolysis is still limited by insufficient electro-catalytic activity and the weak high-temperature chemical adsorption of reactants¹².

In oxide-ion-conducting SOEs, insufficient adsorption of CO_2 in cathode is always a limitation, which leads to the local starvation and then restricts electrolysis performances¹³. The linear CO_2 molecules in the absence of polarity are not easy to be chemically adsorbed and activated, especially at high temperatures. It is common to observe that the local starvation of CO_2 mainly leads to the large electrode polarizations and low current efficiencies for the electrolysis of CO_2 at high temperatures¹⁴⁻¹⁶. Currently preferred chemical adsorption of CO_2 on solid oxide materials is based on grafting a solid amine and producing an alkaline surface; however, the desorption temperature is normally below 500 °C which is far below the operation temperature of SOEs¹⁷⁻²⁰. The defected sites with oxygen vacancies on the surface of solid oxide materials provide the promising possibilities for the chemical adsorption of CO_2 as these sites could act as host sites to accommodate the linear CO_2 molecules, which is expected to significantly extend the onset temperature of chemical desorption of CO_2 and benefit the cathode²¹⁻²². In addition, the chemically adsorbed CO_2 molecules are expected to be strongly activated on these vacancy-related defect sites and consequently favorable for electrochemical reduction at high temperatures.

In this work, the redox-active Mn/Cr with multi-oxidation states is introduced into the B-site of the oxygen excess $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{1.0}\text{O}_{3+\delta}$ and A-site deficient titanates to create the oxygen vacancies both in the bulk and on the surface

for the chemical adsorption of CO₂ molecules. The electrical properties and efficient electrochemical CO₂ splitting are then achieved in the active surface structures on titanate cathode. Direct CO₂ electrolysis is then investigated in the oxide-ion-conducting SOEs at 800 °C.

Experimental

Ceramic oxides including La_{0.2}Sr_{0.8}Ti_{1.0}O_{3+δ} (LST_{O+}), La_{0.2}Sr_{0.8}Ti_{0.9}Cr_{0.1}O_{3+δ} (LSTC_{O+}), La_{0.2}Sr_{0.8}Ti_{0.9}Mn_{0.1}O_{3+δ} (LSTM_{O+}), (La_{0.2}Sr_{0.8})_{0.9}Ti_{0.9}Mn_{0.1}O_{3-δ} (LSTM_{A-}), (La_{0.2}Sr_{0.8})_{0.9}Ti_{0.9}Cr_{0.1}O_{3-δ} (LSTC_{A-}), (La_{0.8}Sr_{0.2})_{0.95}MnO_{3-δ} (LSM) and Ce_{0.8}Sm_{0.2}O_{2-δ} (SDC) powders were synthesized using a solid-state reaction method performed in air²³⁻²⁴.

The phase formations were confirmed by using X-ray diffraction (XRD, Cu Kα, Miniflex600, Rigaku Corporation, Japan) and the data were refined by using the General Structure Analysis System (GSAS) software²⁵. The microstructure of the symmetric cells was investigated by scanning electron microscopy (SEM, SU-8010, JEOL Ltd, Japan). High-resolution transmission electron microscopy (HRTEM, Tecnai F20, FEI Ltd, USA) was also employed to investigate the microstructures of the samples. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo, USA) with monochromatized Al Kα at $h\nu = 1486.6$ eV was utilized to analyze the element states. The TGA tests of the samples were conducted on a thermal analyzer (STA449F3, Netzsch). All infrared spectra were collected with a resolution of 4 cm⁻¹ and 64 scans by a Fourier transform infrared spectrometer (VERTEX 70, Bruker). The powder samples were first reduced in 5% H₂/Ar at 800 °C for 20 h and then treated in CO₂ at 450 °C for 1 h and the *in situ* IR test was subsequently performed. The electrical properties were examined by the DC four-terminal method. The conductivity was measured using an online multi-meter (Keithley 2000, digital multimeter, Keithley Instruments Inc., USA).

The electrolyte-supported symmetric cells with 0.5-mm-thick YSZ electrolyte and different titanate electrodes (1 cm²) were assembled and treated at 1200 °C for 3 h in air. The current collector of the silver paste (SS-8060,

Xinluyi, China) was printed on both surfaces of the electrodes. Silver wire (0.2 mm in diameter) was used as the lead wire and attached to the Ag current collector using conductive adhesive (DAD87, Shanghai Research Institute for Synthetic Resins, China) and treated at 550 °C for 30 min in air. The 0.5-mm-thick YSZ-supported single SOEs with titanate cathodes (1 cm²) and LSM anode (1 cm²) were assembled and treated at 1200 °C for 3 h in air. Electrochemical measurement of the cells was performed using an electrochemical station (IM6, Zahner, Germany) with a frequency range of 4 MHz to 100 mHz and a voltage perturbation of 10 mV. The gas flow was controlled with the mass flow meters (D08-3F, Sevenstar, China). The electrolysis cells were sealed into a homemade testing jig using ceramic paste (JD-767, Jiudian, China) for the electrochemical test. The electrolysis experiment was conducted by flowing 5% H₂/Ar at the flow rate of 50 mL min⁻¹ for 1.5 h and then pure hydrogen at the flow rate of 50 mL min⁻¹ was supplied to the cathode for 2.0 h at the operation temperature. After that, the cathode would be sufficiently reduced and activated. CO₂ electrolysis was subsequently performed using an electrochemical station at different applied voltages (1.4, 1.6 and 1.8 V) with pure CO₂ (50 mL min⁻¹) fed into the cathode. The CO production was analyzed by using an online gas chromatograph (GC2014, Shimazu, Japan) for the exhaust stream from the electrolyzers at 800 °C.

Results and discussion

Different perovskite defect chemistries and their combinations such as oxygen excess, A-site deficiency and Mn/Cr doping have been investigated, seeking to optimize electrolysis cathode properties. XRD analysis confirms the synthesis of pure-phase perovskite powders. The patterns are shown in Fig. 1(a) and (b). All oxidized samples could be indexed assuming a cubic symmetry, with space group *Pm-3m*. As shown in Fig. 1(c) and (d), on reduction, a unit cell expansion is observed due to the reductions of Ti and Mn. This is because most of the Mn⁴⁺ (0.530 Å) and part of the Ti⁴⁺ (0.605 Å) have been reduced to Mn³⁺ (0.645 Å) and Ti³⁺ (0.670 Å). Due to the A-site

deficiency, the perovskite structure is retained for the titanate phase, suggesting structural redox stability. The doping and reduction of Mn/Cr should be coupled with the creation of additional oxygen vacancies in the titanate, which in turn should facilitate CO₂ chemisorption. XPS furthermore confirms the presence of the reduced species Ti³⁺ and Mn³⁺ within the reduced LSTM_{A-}, corroborating the XRD results. As shown in Fig. 2(a), only Ti⁴⁺ is observed in the oxidized LSTM_{A-}; however, part of the Ti⁴⁺ is chemically reduced into Ti³⁺ by treating the LSTM_{A-} in a reducing atmosphere due to the peak shift²⁶⁻²⁷. The lower valence states of Ti³⁺, Mn^{4+/3+} are present in reduced samples while most of the element is at high oxidation state in the oxidized samples.

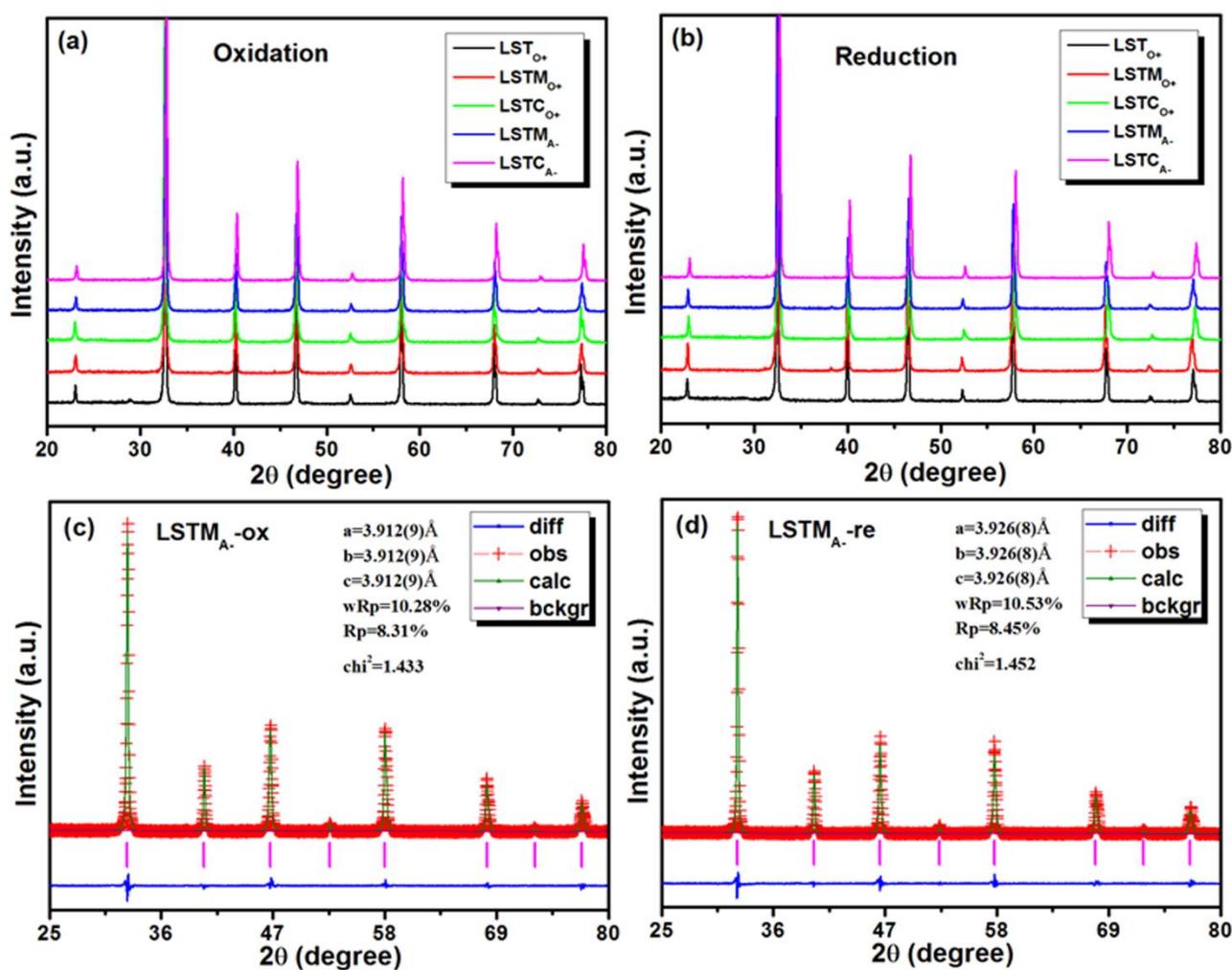


Fig. 1 XRD patterns of (a) oxidized and (b) reduced LST_{O+}, LSTM_{O+}, LSTC_{O+}, LSTM_{A-} and LSTC_{A-}; XRD

Rietveld refinement of (c) oxidized and (d) reduced LSTM_{A-}.

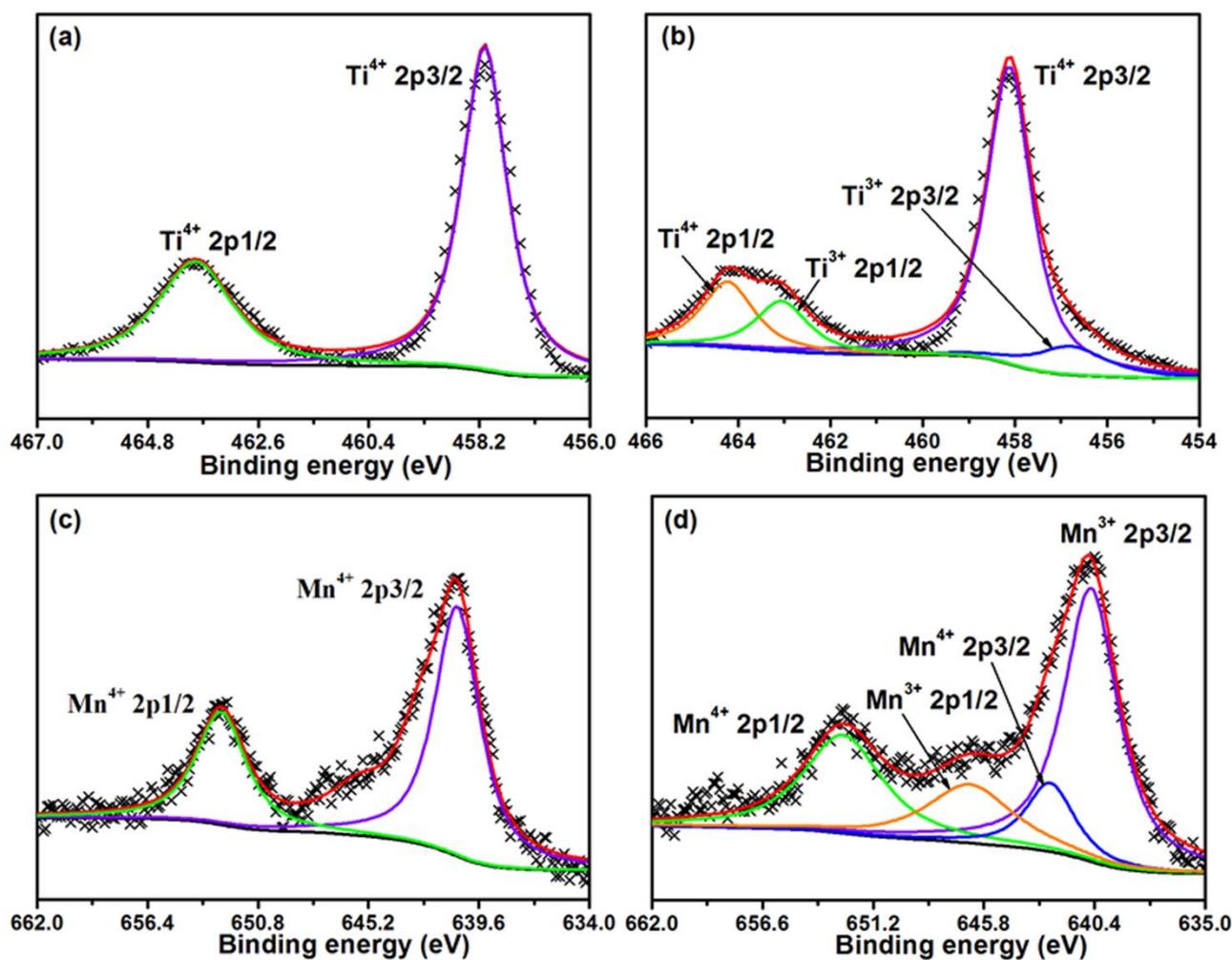


Fig. 2 XPS results for (a) Ti and (c) Mn in the oxidized LSTMA₋; (b) and (d) in the reduced LSTMA₋.

HRTEM analysis of the oxidized and reduced LSTMA₋ has revealed lattice spacing of 0.289 nm (110) and 0.278 nm (110), respectively, as shown in Fig. 3(a) and (b), consistent with the separation spacing determined by the XRD analysis. The differences of ionic radius may contribute to the changes of the lattice spacing. Thermogravimetric analysis on the various titanates, as shown in Fig. 4(a), suggests varying degrees of oxygen stoichiometry, depending on titanium substitution with Cr/Mn and A-site deficiency. Whereas LSTO₊ shows a change of 0.033 mol of oxygen upon oxidation/reduction, the Cr and Mn substituted stoichiometries release/absorb 0.041 and 0.057 mol of lattice oxygen for the LSTCO₊ and LSTMO₊, confirming the reducibility of the Mn and consequent formation of additional oxygen vacancies upon reduction. However, the Cr³⁺ in titanate lattice is less reducible that leads to

similar oxygen absorption for reduced LST_{O^+} and LSTC_{O^+} samples. Strong reduction only produces partial transition of Cr^{3+} to Cr^{2+} as confirmed by the larger weight gains in TGA analysis. The weight changes increase even further upon A-site deficiency, suggesting that more oxygen vacancies of 0.060 and 0.073 mol are created for the LSTC_{A^-} and LSTM_{A^-} , respectively. The varying oxygen contents and abilities to store and release lattice oxygen also manifest themselves in the oxide ionic conductivities of the titanates. The ion conductivity of sintered pellets is tested using the electron-blocking electrode method for the reduced states²⁸⁻²⁹. As shown in Fig. 4(b), reduced LST_{O^+} has lowest ionic conductivity, reaching $9.6 \times 10^{-4} \text{ S cm}^{-1}$ at 800 °C. Upon substitution with Cr/Mn and consequently increasing oxygen vacancy concentration under reducing conditions, this increases by an order of magnitude to 6.1×10^{-3} and $6.4 \times 10^{-3} \text{ S cm}^{-1}$ for the LSTC_{O^+} and LSTM_{O^+} , respectively. Introducing A-site deficiency causes an additional 20% increase to 7.4×10^{-3} and $8.2 \times 10^{-3} \text{ S cm}^{-1}$ for the LSTC_{A^-} and LSTM_{A^-} under identical conditions. It is expected that the oxygen vacancy defect sites are able to accommodate carbon dioxide molecules to exhibit the chemical adsorption behavior.

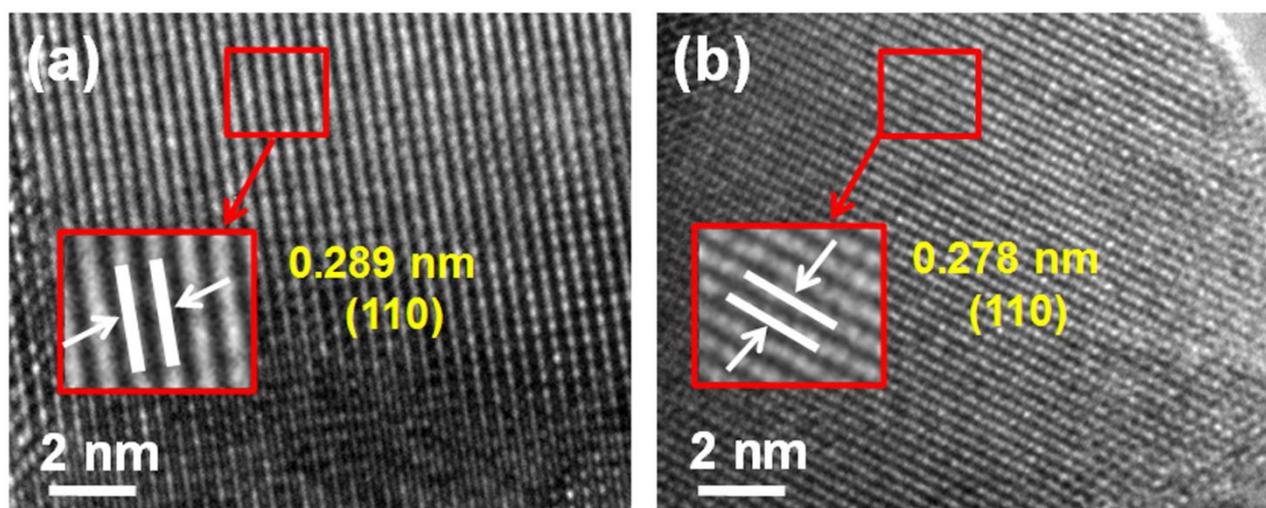


Fig. 3 HRTEM results for the (a) oxidized and (b) reduced LSTM_{A^-} .

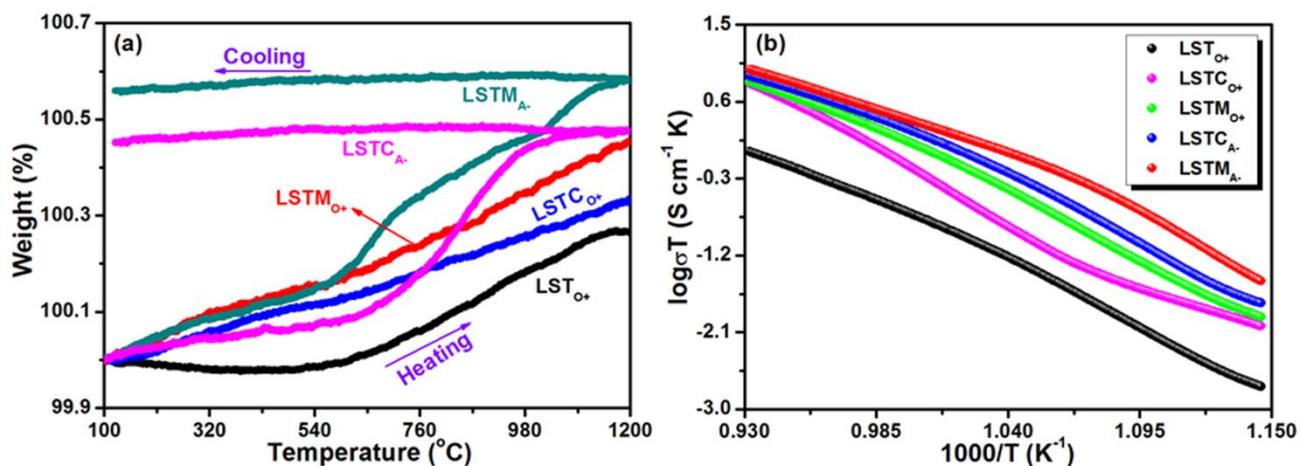


Fig. 4 (a) TGA tests of the reduced samples (800 °C for 20 h in 5% H₂/Ar) from 100 to 1200 °C in air; (b) The dependence of ionic conductivity on temperature of the reduced samples in 5% H₂/Ar.

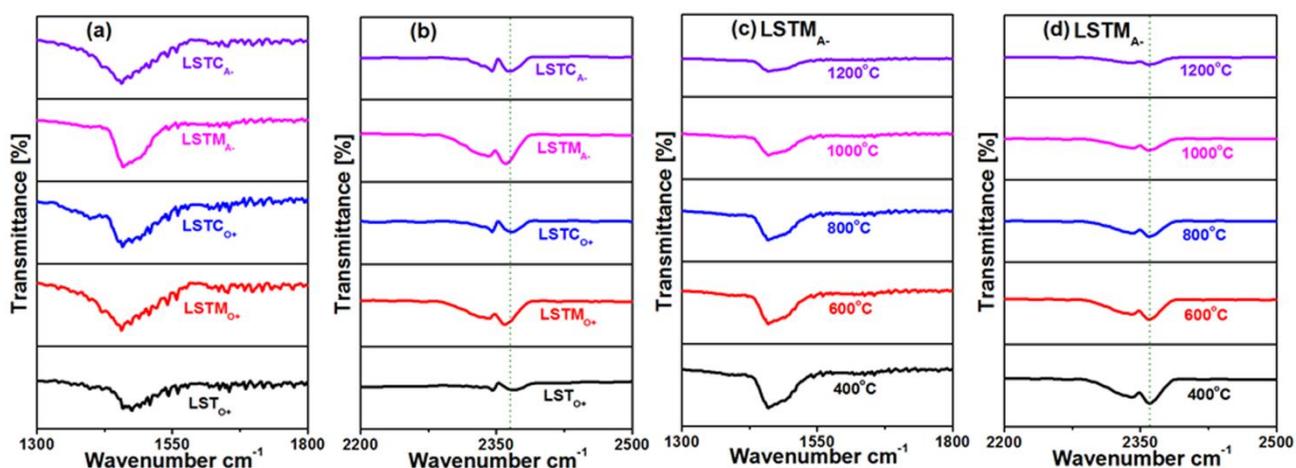


Fig. 5 (a) and (b) *in situ* IR spectra of CO₂ adsorbed on the reduced samples at room temperatures; (c) and (d) *in situ* IR spectra of CO₂ adsorbed on the reduced LSTM_{Ax} from 400 to 1200 °C.

The chemical adsorption of CO₂ molecules on reduced titanate samples was investigated by *in situ* IR spectroscopy.

All samples with adsorbed CO₂ show absorption signals in two distinct IR bands at room temperature in Fig. 5(a) and (b), i.e. 2380 – 2300 cm⁻¹, which is associated with CO₂ molecules³⁰ on the sample surface and 1500 – 1430 cm⁻¹, which is typically observed for CO₃²⁻³¹. The chemisorbed carbon dioxide on the titanate surface is therefore assumed to be intermediate between molecular CO₂ and carbonate ions. As expected from the concentration of oxygen ion vacancies, which should translate into an active oxide surface, the strongest IR absorption is observed

for the LSTM_A and LSTC_A . To test the ability to adsorb CO_2 at elevated temperature, LSTM_A was subjected to *in situ* IR tests between 400 and 1200 °C. As shown in Fig. 5(c) and (d), the strong chemical adsorption is still present even at 1200 °C, indicating the successful chemical CO_2 adsorption through control of oxygen vacancies and A-site deficiency. It is worth noting that both signals of carbonate and CO_2 molecules exist even at such high temperature, indicative of the presence of strong chemical adsorption of CO_2 on defected structure of titanate oxide.

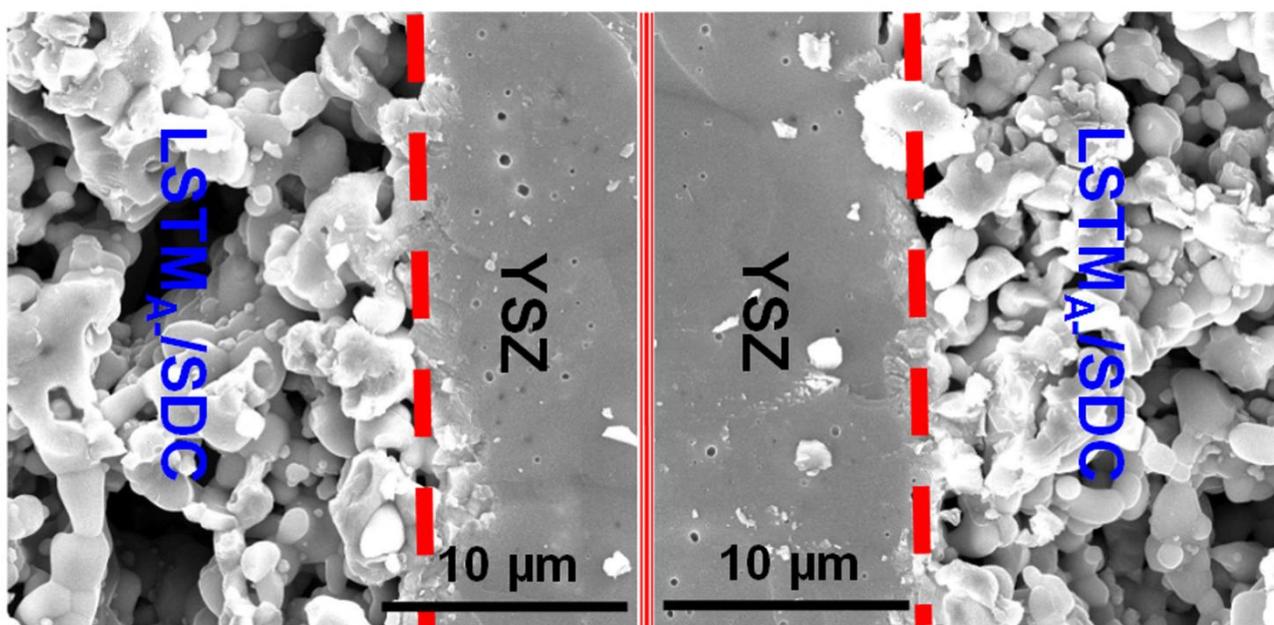


Fig. 6 Enlarged view of the electrode/electrolyte interfaces of the cross-sectional SEM images of the solid oxide symmetric cell with the cell configuration of $\text{LSTM}_A/\text{SDC}-\text{YSZ}-\text{LSTM}_A/\text{SDC}$.

Symmetrical electrolyser cell was fabricated, using composite titanate cathode with SDC. SDC is incorporated in the cathode since it has superior ionic conductivity and is expected to deliver oxygen ion transport while the titanate provides electronic conductivity. Cross section of the cell can be found in Fig. 6, showing porous electrodes and dense electrolytes. AC impedance was performed on the symmetrical cells to assess the electrode polarization behaviour under reducing conditions, with $p\text{H}_2$ ranging from 0.20 – 1.0 bar. For all titanates it was found that the series resistance R_s mainly comes from ionic resistance of the YSZ electrolyte, was generally stable in a wide range of $p\text{H}_2$. In this case, the series resistance R_s has been set as 0 to compare the polarization resistances R_p . As shown

in Fig. 7(a), the R_p of the symmetric cell based on LSTO_+ decreases from 4.06 to 1.97 $\Omega \text{ cm}^2$ with increasing $p\text{H}_2$ ranging from 0.20 – 1.0 bar, which suggests that a stronger reducing atmosphere is beneficial for improving the electrode polarization. R_p for $\text{LSTM}_{\text{O}+}$ and $\text{LSTC}_{\text{O}+}$ decreases with increasing hydrogen concentration from 2.11 to 1.27 $\Omega \text{ cm}^2$ and 2.76 to 1.38 $\Omega \text{ cm}^2$, respectively, which is probably due to the enhanced charge transfer and species diffusion in titanate electrodes^{21, 32}. In contrast, R_p for $\text{LSTM}_{\text{A}-}$ and $\text{LSTC}_{\text{A}-}$ significantly decreases from approximate 1.95 to 0.94 $\Omega \text{ cm}^2$ ($p\text{H}_2$: 0.20 – 1.0 bar) and 1.99 to 1.07 $\Omega \text{ cm}^2$, respectively, as the hydrogen concentration is increased, which again validates the enhancement of electrode activity by creation of oxygen vacancy in the lattice and A-site deficiency. The symmetrical cell results are summarized in Fig. 7(f), and $\text{LSTM}_{\text{A}-}$ and $\text{LSTC}_{\text{A}-}$ perform the best in $p\text{H}_2 = 1.0$ bar, which are lower than the other samples.

The direct electrolysis of pure CO_2 is studied in solid oxide electrolyzers with 5 types of cathodes under a series of applied voltages ranging from 1.0 to 2.0 V at 800 °C. The open circuit voltage (OCV) of the cells was established by exposing the cathode and anode to pure H_2 and static air, respectively, and was found to reach 1.1 V, indicating good gas separation by the cells. Typical current – voltage (I - V) curves for the various cathode materials in direct CO_2 electrolysis mode are shown in Fig. 8(a). As expected from the previous findings, LSTO_+ shows the poorest performance, reaching a maximum current density of 0.25 A cm^{-2} at 2.0 V. Improved performance is observed for Mn/Cr substituted compositions, which can be attributed to enhanced CO_2 adsorption and activation at high temperatures. $\text{LSTM}_{\text{O}+}$ reaches a maximum current density of 0.52 A cm^{-2} at 2.0 V. The A-site deficiency shows a further improvement, with maximum current densities of 0.68 and 0.57 A cm^{-2} at 2.0 V for $\text{LSTM}_{\text{A}-}$ and $\text{LSTC}_{\text{A}-}$, respectively. As shown in Fig. 8(b), the stable current density with the $\text{LSTM}_{\text{A}-}$ cathode reaches 0.25, 0.40 and 0.54 A cm^{-2} at 1.4, 1.6 and 1.8 V, respectively. Similarly, the stable current density with $\text{LSTC}_{\text{A}-}$ cathode reaches 0.22, 0.32 and 0.46 A cm^{-2} at 1.4 – 1.8 V, respectively; these values are 1.8 – 2.2 times higher in contrast to the cell with the LSTO_+ cathode under the same conditions, which further indicates that the more oxygen vacancies and A-site

deficiency on electrode materials have played a significant role in promoting the process of CO₂ electrolysis.

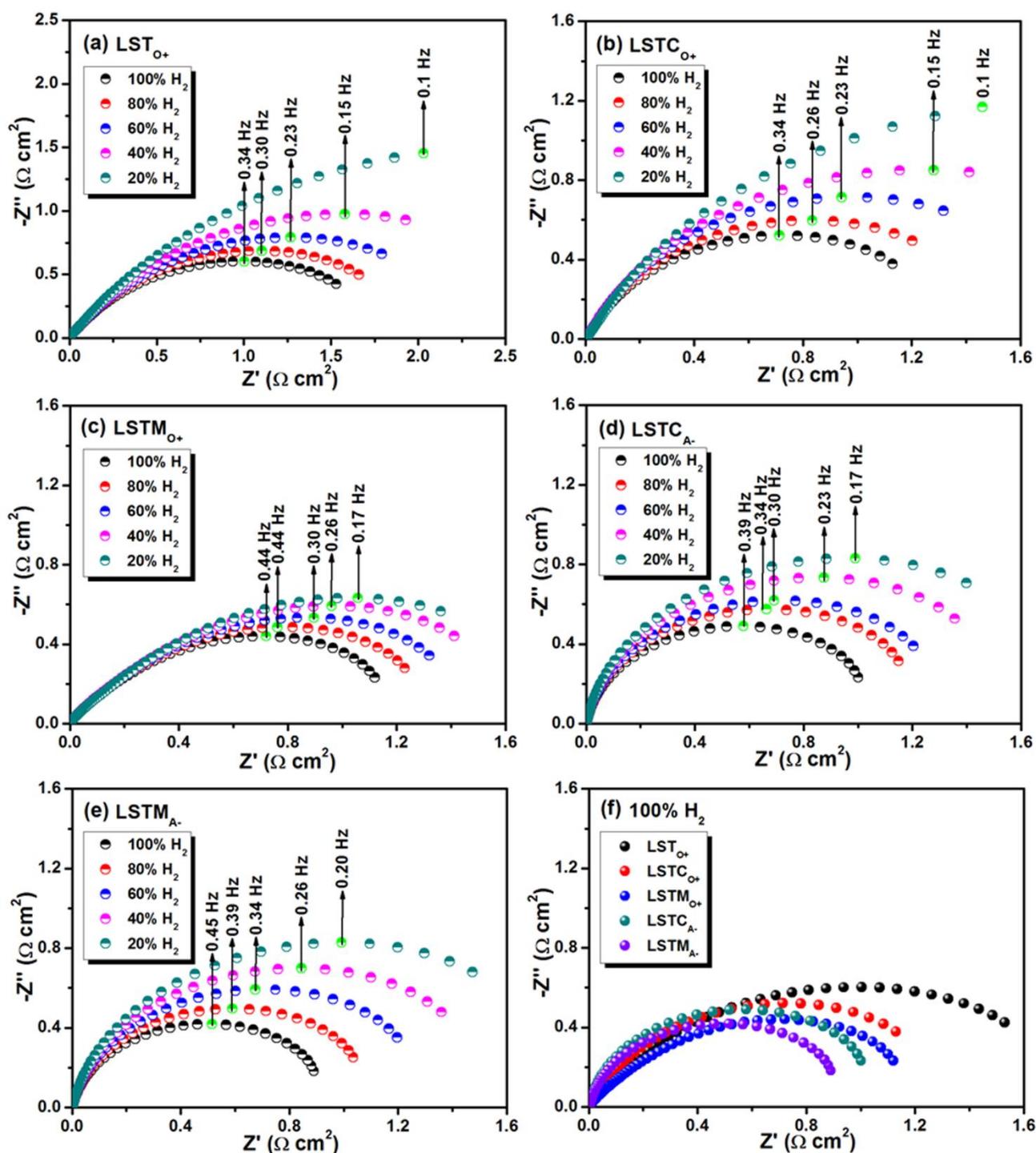


Fig. 7 AC impedance spectra of the symmetric cells for (a) LST_{O+}, (b) LSTC_{O+}, (c) LSTM_{O+}, (d) LSTC_{A-} and (e) LSTM_{A-} at various H₂ partial pressures at 800 °C; (f) AC impedance spectra of the symmetric cells with different electrodes in 100% H₂.

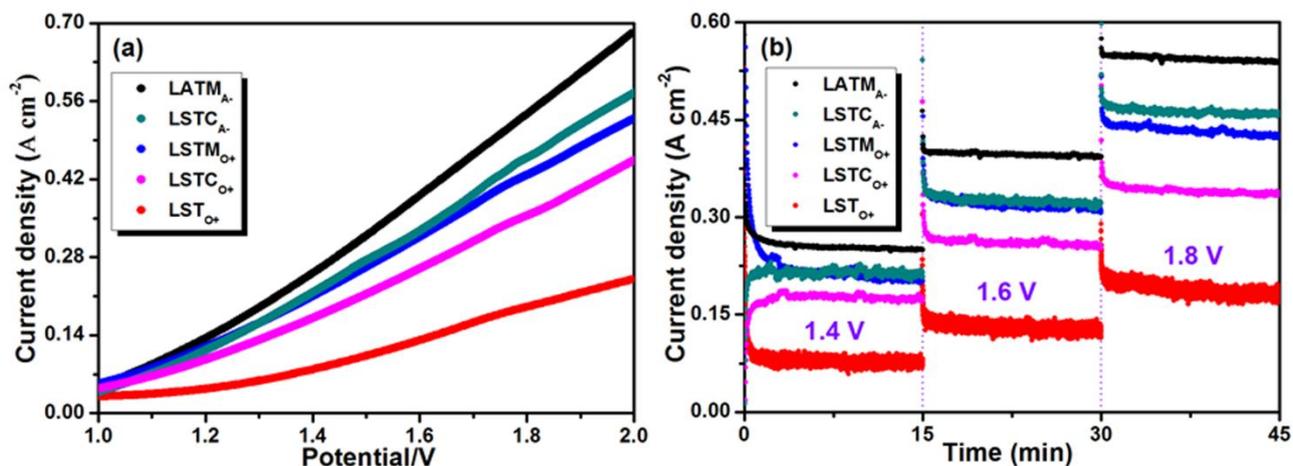


Fig. 8 (a) I - V curves of CO₂ electrolysis with different cathodes at 800 °C; (b) Short-term performances of CO₂ electrolysis at different voltages.

To further understand the observed electrochemical performance in CO₂ electrolysis mode at 800 °C for the different cathode materials, impedance spectroscopy was carried out under a range of applied biases, i.e. 1.4 – 1.8 V. Similar trends are observed for all cathode materials in Fig. 9. It is observed that the R_s values are generally stable, whereas the R_p values obviously decrease as the applied voltages increase from 1.4 to 1.8 V. Increasing the voltage is expected to improve electrode polarization, following the improved kinetic process of the electrode. The applied voltage electrochemically reduces the composite cathode to enhance the conductivity and hence accordingly enhances the electrocatalytic activity of the composite electrode. At low frequency, the mass transfer especially for LST_{O+} cathode dominates the electrode process due to the dissociative adsorption, gas conversion and species transfer at the three-phase boundary (TPB). The R_p with LST_{O+} cathode improves from 1.43 to 0.92 Ω cm² at 1.4 to 1.8 V, respectively, suggesting improved gas conversion kinetics at high voltages. The R_p with LSTM_{O+} cathode is reduced from 1.08 Ω cm² at 1.4 V to 0.64 Ω cm² at 1.8 V, because of the enhanced ionic conduction and chemical CO₂ adsorption. In contrast, The R_p with LSTM_{A-} cathode significantly decreases to 0.82 Ω cm² at 1.4 V and is further reduced to 0.48 Ω cm² at 1.8 V, which demonstrates the A-site deficiency would further produce higher oxygen vacancy concentration that is beneficial to electrode activity enhancement³³. Similar behavior has also been

observed for LSTC_{O+} and LSTC_{A-} cathodes. The catalytic activity of Mn itself in ABO₃ oxide is better than the Cr-doped sample, and the ionic conductivity of LSTM_{A-} is higher than that of LSTC_{A-}. The above two points would accordingly deliver better performance for LSTM_{A-} electrode even though LSTC_{A-} has a higher oxygen vacancy concentration. The impedance spectra of different cathode materials' at 1.8 V are summarized in Fig. 9(f).

Further evidence of these titanates' suitability to reduce CO₂ at the cathode comes from inspecting the rate of CO production as measured by gas chromatography and corresponding current efficiencies at different applied voltages, as shown in Fig. 10. The lower current efficiency may be because of the transport of impurity charge carriers in the oxide ceramic electrolyte especially the oxide ions and electrons. The maximum CO productions for the cell based on the LSTM_{A-} and LSTC_{A-} electrodes are approximately 3.66 and 3.03 mL min⁻¹ cm⁻², respectively, which are 100-200% higher than 2.80, 2.27 and 1.12 mL min⁻¹ cm⁻² for LSTM_{O+}, LSTC_{O+} and LST_{O+} electrodes at 1.8 V, respectively. In addition, the maximum current efficiencies with LSTM_{A-} and LSTC_{A-} cathodes are increased to 96.8% and 94.5% under the same conditions, again confirming the enhanced cathode activity with more oxygen vacancies. Results have been summarized in Table 1. In order to validate the long-term stability of the LSTM_{A-} cathode, direct CO₂ electrolysis is performed at a fixed voltage of 1.4 V and 800 °C for 100 h with pure CO₂ fed in the cathode. As shown in Fig. 10(c), the current density with LSTM_{A-} cathode is stabilized at 0.25 A cm⁻² with close to 100% current density in the long-term test at high temperature, which confirms excellent stability of LSTM_{A-} cathode with A-site deficiency and Mn-doping titanate for direct CO₂ electrolysis. To further investigate the cycling performance, the LSTM_{A-} cathode is *in situ* repeatedly treated at 800 °C in a 5% H₂/Ar or air and then tested for CO₂ splitting at 1.4 V for 1.5 h. The results show that the cell with LSTM_{A-} cathode still demonstrates a comparable performance even after 3 redox cycles in Fig. 10(d). A-site deficiency together with B-site doping not only produces high temperature stability but also substantially enhances redox cycling performances for high temperature CO₂ electrolysis.

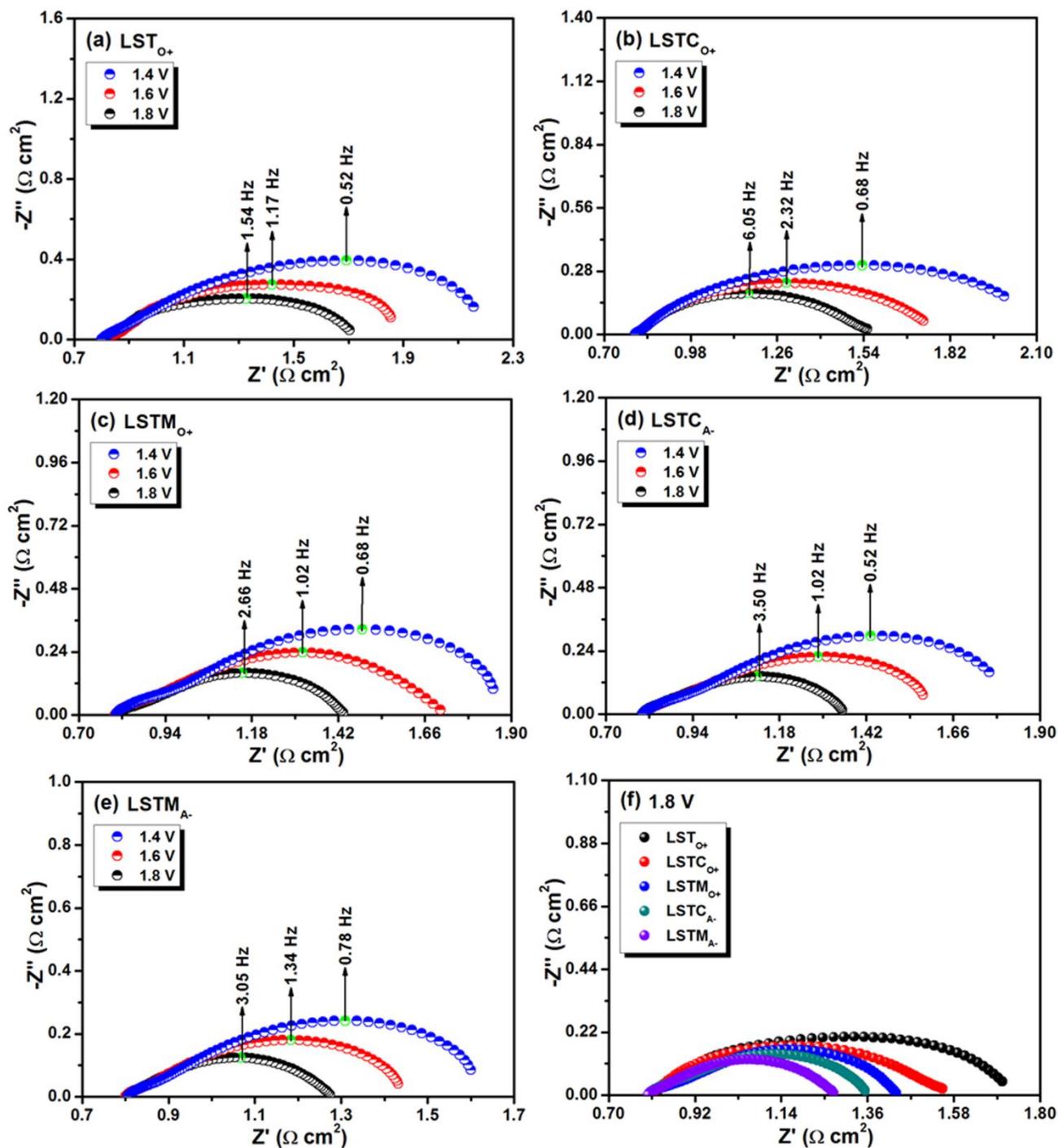


Fig. 9 *In situ* AC impedance spectra for electrolyzers for different cathodes (a) LST_{O₊}, (b) LSTC_{O₊}, (c) LSTM_{O₊}, (d) LSTC_{A₋} and (e) LSTM_{A₋} at various voltages; (f) *In situ* AC impedance spectra for electrolyzers with different cathodes at 1.8 V with the flow of CO₂ at 800 °C.

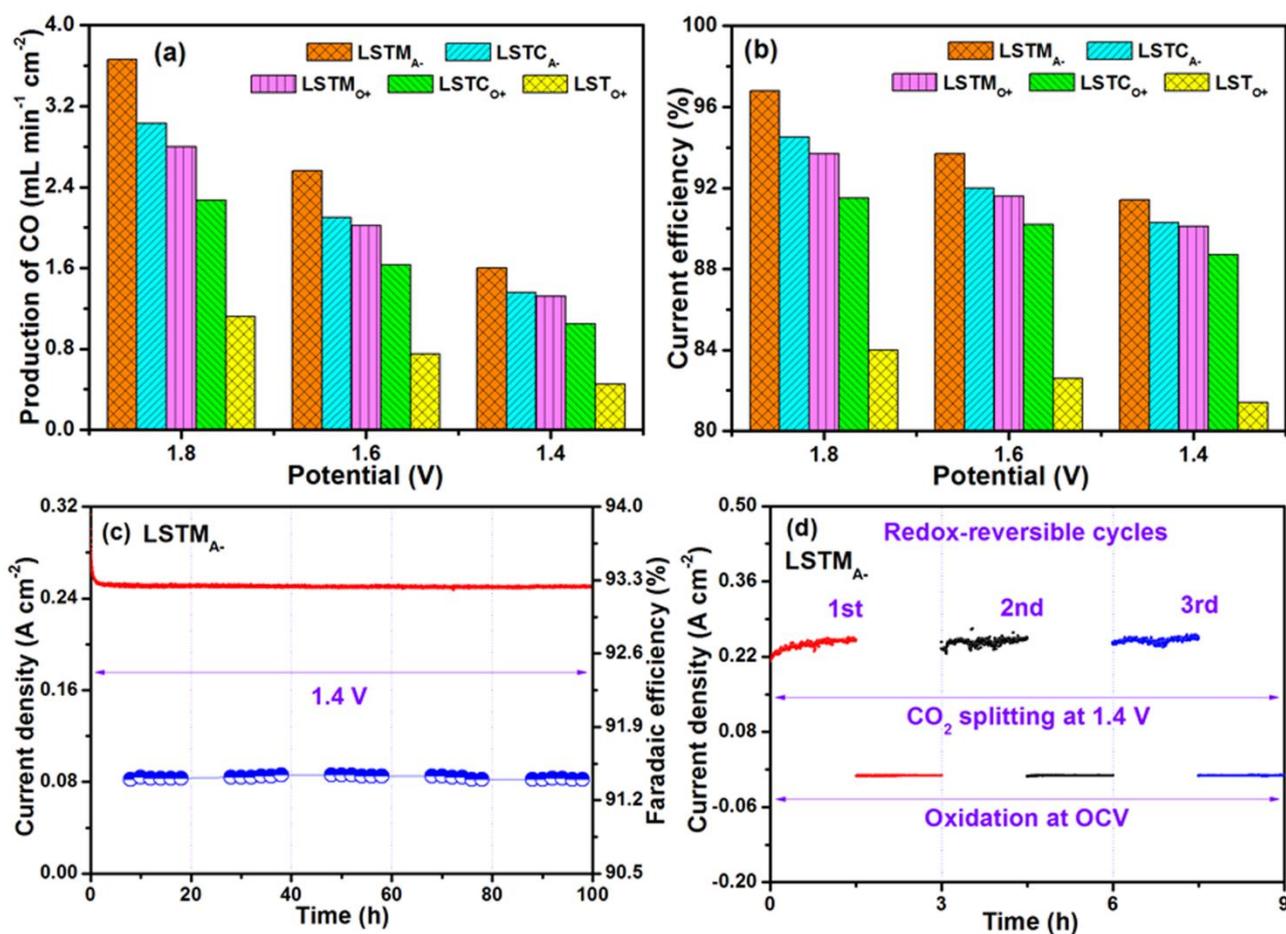


Fig. 10 (a) CO production and (b) current efficiency with different cathodes; (c) Long-term performance and current efficiency of the LSTM_{A-} cathode with the flow of CO₂ at 800 °C; (d) Short-term performance of LSTM_{A-} cathode after 3 redox cycles.

Table 1 The comparison of CO₂ electrolysis with different cathode at different applied voltages.

| Cathode | | Applied voltage (V) | | |
|--------------------|--|---------------------|------|------|
| | | 1.4 | 1.6 | 1.8 |
| LSTO ₊ | CO production (mL min ⁻¹ cm ⁻²) | 0.45 | 0.75 | 1.12 |
| | Current efficiency (%) | 81.4 | 82.6 | 84.0 |
| LSTCO ₊ | CO production (mL min ⁻¹ cm ⁻²) | 1.05 | 1.63 | 2.27 |
| | Current efficiency (%) | 88.7 | 90.2 | 91.5 |
| LSTMO ₊ | CO production (mL min ⁻¹ cm ⁻²) | 1.32 | 2.02 | 2.80 |
| | Current efficiency (%) | 90.1 | 91.6 | 93.7 |
| LSTCA ₋ | CO production (mL min ⁻¹ cm ⁻²) | 1.36 | 2.10 | 3.03 |
| | Current efficiency (%) | 90.3 | 92.0 | 94.5 |
| LSTMA ₋ | CO production (mL min ⁻¹ cm ⁻²) | 1.60 | 2.56 | 3.66 |
| | Current efficiency (%) | 91.4 | 93.7 | 96.8 |

Conclusions

In summary, the remarkable chemical adsorption/activation of CO₂ at high temperature has been achieved by introducing more oxygen vacancies in Mn/Cr-doped and A-site deficient titanates. The ionic conductivities of A-site deficient and B-site doped titanates are greatly improved in reducing atmosphere. In addition, these titanates significantly enhance the cathode performances of CO₂ electrolysis and further exhibit high temperature stability as well as significant redox cycling ability. This study demonstrates that these titanates are promising candidates as alternative cathode materials in solid oxide electrolyzers, providing the tools to develop next generations electrochemical devices for energy conversion and storage.

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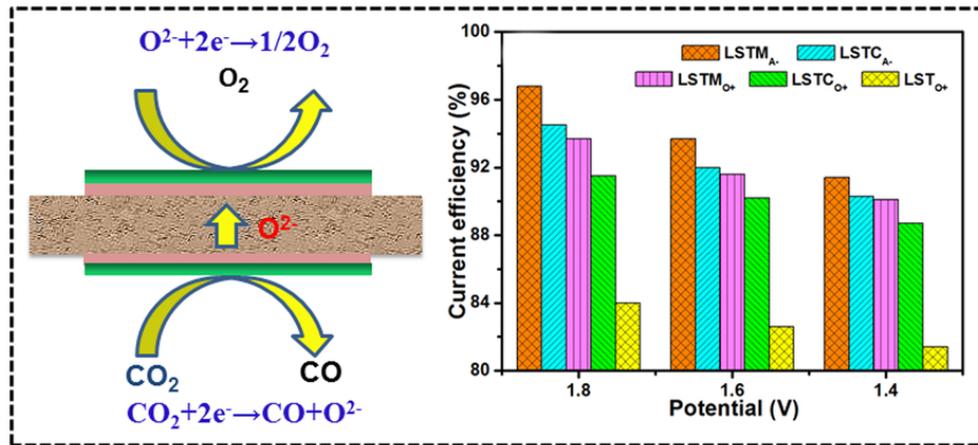
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Highlights

The remarkable cathode performances of CO₂ electrolysis have been achieved by introducing more oxygen vacancies in Mn/Cr-doped and A-site deficient titanates.



79x36mm (300 x 300 DPI)