Enhancing CO$_2$ electrolysis through synergistic control of non-stoichiometry and doping to tune cathode surface structures

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Sustainable future energy scenarios require significant efficiency improvements in both electricity generation and storage. High-temperature solid oxide cells, and in particular carbon dioxide electrolysers, afford chemical storage of available electricity that can both stabilize and extend the utilization of renewables. Here we present a double doping strategy to facilitate CO$_2$ reduction at perovskite titanate cathode surfaces, promoting adsorption/activation by making use of redox active dopants such as Mn linked to oxygen vacancies and dopants such as Ni that afford metal nanoparticle exsolution. Combined experimental characterization and first-principle calculations reveal that the adsorbed and activated CO$_2$ adopts an intermediate chemical state between a carbon dioxide molecule and a carbonate ion. The dual doping strategy provides optimal performance with no degradation being observed after 100 h of high-temperature operation and 10 redox cycles, suggesting a reliable cathode material for CO$_2$ electrolysis.
Solid oxide electrolysers (SOEs) have been attracting great interest due to their high efficiencies in converting low-carbon fuels from renewable electrical energy.1-3 They can exploit available high-temperature heat streams from nuclear plants or exhaust industry heat to maximize electrical efficiency and both thermodynamic and kinetic advantages can be anticipated because of the high operating temperatures.4-6 In SOEs, using an externally applied potential, CO₂ can be electrochemically converted into CO and O₂ at the cathode, while the generated O₂⁻ ions transport through the electrolyte to the anode to form O₂ gas.1,5,6 Currently, nickel/yttria-stabilized zirconia (Ni-YSZ) composites are the cathode of choice for high-temperature SOEs.5,6 In such a composite, the percolating networks of both Ni and YSZ provide sufficient electronic and ionic conductivity, while the Ni guarantees high electrocatalytic activity towards the reduction reaction. Long-term operation with Ni-YSZ is feasible only in CO/CO₂ gas mixtures, where the presence of CO maintains a reducing atmosphere. Under realistic conditions however, reduction-oxidation (redox) cycles of Ni will inevitably occur in the cathode, ultimately leading to electrode degradation and delamination.8,9 In contrast, redox-stable ceramic cathodes would offer a promising alternative for direct high-performance CO₂ electrolysis. Especially materials exhibiting n-type conduction properties are expected to demonstrate improved conductivity under the strongly reducing cathode conditions. Perovskite-type doped strontium titanates, (La,Sr)TiO₃ (LSTO), are such materials, due to the reducibility of Ti⁴⁺ to Ti³⁺, and have therefore attracted a significant amount of interest within the field of SOE and fuel cell technologies.10,11 A composite cathode based on La₀.₂Sr₀.₈Ti₁.₀O₃⁺δ was shown to be well adapted to direct CO₂ electrolysis,12 because the titanate is partially electrochemically reduced (Ti⁴⁺ → Ti³⁺) at potentials required for CO₂ reduction and the n-type electronic conduction is accordingly enhanced, but cathode performance for CO₂ electrolysis is still limited by insufficient electro-catalytic activity and the weak high-temperature chemical adsorption of reactants.13

The incorporation of catalytically active metal nanoparticles through impregnation methods has proven to be an effective approach to enhance ceramic electrode activity.14 However, long-term stability of nanocatalysts at high operating temperature remains a major challenge due to particle agglomeration leading to performance degradation.16,17 An alternative method is to incorporate the metal element as a dopant within the host lattice during the synthesis of the catalyst in air, which is then exsolved at the surface in the form of catalytically active metallic nanoparticles under reducing conditions. If the composition and conditions are carefully chosen to avoid full decomposition, anchored nanoparticles can be grown on the cathode. Any possible agglomeration of exsolved Ni nanoparticles on the substrate surface can be remedied by periodically cycling from oxidizing to reducing conditions.11 We have recently demonstrated the in situ growth of metal nanoparticles directly from a perovskite backbone support through control of composition, particularly by tuning deviations from the ideal ABO₃ stoichiometry.18 The exsolved metal nanoparticles exhibit enhanced high-temperature stability and improved coking resistance, due to a stronger metal–oxide interface resulting from an anchoring effect with the parent perovskite. The key surface effects and defect interactions of exsolution-based perovskite materials are expected to demonstrate promising catalytic functionalities.19

High-temperature CO₂ electrolysis suffers from poor adsorption and activation of the reactant, due to the linear molecules lacking polarity. This is believed to cause local starvation of CO₂ in SOE cathodes.1,3,7,12 Currently, preferential chemical adsorption of CO₂ on solid oxide materials is based on grafting solid amines, which produces an alkaline surface. However, the desorption temperature is normally below 500 °C, which is far below typical electrolyser operating temperatures. Surface oxygen vacancies created next to redox active sites on solid oxide materials may provide alternative sites for CO₂ chemisorption and are expected to significantly elevate the onset temperature of chemical desorption of CO₂, which would benefit cathode performance.22 Combining oxygen vacancies and exsolved catalytic nanoparticles should finally produce an active interface for electrocatalytic CO₂ reduction.

In this work, active nanostructures are investigated on titanate surface under differing regimes of perovskite non-stoichiometry. The exsolved metal nanoparticles coupled with tailored oxygen vacancies through Cr and Mn substitution produce a strongly interactive interface. Chemical adsorption/activation of CO₂ is investigated on these titanate surfaces as well as their effectiveness as cathode materials for indirect CO₂ electrolysis.

Results

Crystal structure and microstructure. Different perovskite-defect chemistries and their combinations have been investigated, (oxygen excess, cation deficient and Sr/Cr doped) seeking to optimize electrolysate cathode properties. X-ray diffraction analysis confirms the synthesis of pure-phase La₀.₂Sr₀.₈Ti₁.₀O₃⁺δ (LSTO⁺δ), La₀.₂Sr₀.₈Ti₀.₉Cr₀.₁O₃⁺δ (LSTC), La₀.₂Sr₀.₈Ti₀.₉Mn₀.₁O₃⁺δ (LSTM), La₀.₂Sr₀.₈Ti₀.₉Cr₀.₂Mn₀.₈O₃⁺δ (LSTCMA), La₀.₂Sr₀.₈Ti₀.₉Cr₀.₂Mn₀.₈O₃⁻δ (LSTCNA), La₀.₂Sr₀.₈Ti₀.₉Cr₀.₂Mn₀.₈O₃⁺δ (LSTCNA) and La₀.₂Sr₀.₈Ti₀.₉Cr₀.₂Mn₀.₈O₃⁻δ (LSTCNA) powders (Fig. 1). The patterns are shown in Supplementary Section (Supplementary Fig. 1a,b). All oxidized samples could be indexed assuming a cubic symmetry, with space group Pm-3m. As shown in Supplementary Figs 1 and 2 and Supplementary Table 1, on reduction, a unit cell expansion is observed due to the reductions of Ti, Mn and Cr (from M⁴⁺ to M³⁺/²⁺). 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. The LSTO⁺δ is oxygen-excess while the oxygen with δ amount is present in the form of oxygen interstitial in perovskite oxide. However, the (La,Sr)(Ti,Mo)O₃⁺δ (M=Mn, Cr) has redox-active dopants such as Mn linked to oxygen vacancies even though the interstitial oxygen might be still present after reduction. The nickel containing compounds LSTMN⁺ and LSTCN⁻ exhibit nickel exsolution on reduction, as observed in X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and microscopy. Supplementary Fig. 2 shows the emergence of a peak at 2θ = 44.5⁰, corresponding to cubic metallic nickel. Due to the A-site deficiency, the perovskite structure is retained for the titanate phase, suggesting structural redox stability. XPS on oxidized and reduced samples shows that nickel is only present as Ni²⁺ in the former, whereas metallic Ni⁰ is additionally present in the latter, corroborating the X-ray diffraction results. XPS furthermore confirms the presence of the reduced species Ti⁴⁺, Mn²⁺ and Cr³⁺/²⁺ within the reduced titanates (Supplementary Figs 3 and 4). Figure 2a,b present scanning electron microscopic micrographs of sintered LSTMN⁺ pellets after reduction, showing uniform titanate surface decoration with Ni nanoparticles. The titanates exist with an average of 60 nm, which should narrow highly active as electrocatalyst. The growth of these Ni nanoparticles was studied using high-resolution transmission electron microscopy. From the lattice spacings in Fig. 2c,d, 0.275 and 0.203 nm, it becomes clear that two distinct phases have emerged, that is, reduced titanate (110) and metallic nickel (111), respectively.
A clear hetero-junction is visible between the two phases, suggesting a strong interaction between the titanate backbone and exsolved nanoparticles. This anchoring effect is expected to provide enhanced thermal stability of the catalyst, preventing the severe long-term agglomeration which is commonly observed for impregnated catalysts. Regeneration of the nanoparticles is also possible through periodic redox cycling. Besides, selected-area electron diffraction analysis for the reduced LSTMNA is shown in Supplementary Fig. 5, it shows that LSTMNA is able to produce the polycrystalline structure.

Oxygen nonstoichiometry and conductivity. Thermogravimetric analysis on the various titanates, as shown in Supplementary Fig. 6 and Supplementary Table 2, suggests varying degrees of oxygen stoichiometry, depending on titanium substitution with Cr/Mn/Ni. Whereas LSTO shows a change of 0.032 mol of oxygen upon oxidation/reduction, the Cr- and Mn-substituted titanates release/absorb 0.039 and 0.056 mol of lattice oxygen, confirming the reducibility of the Mn and consequent presence of Ni nanoparticles coupled with a large concentration of oxygen vacancies.

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 the dense perovskite structure and confirms that creating additional oxygen ion vacancies should indeed be beneficial for ionic transport by increasing the concentration of charge carriers.

CO2 adsorption and activation. The chemical adsorption of CO2 molecules on reduced titanate samples was investigated by in situ infrared spectroscopy. The infrared scans for all the samples without CO2 adsorption at room temperature are shown...
in Supplementary Fig. 9a,b, in which no CO2 or carbonate species (CO$_3^{2-}$) signals are observed. In contrast, all samples with adsorbed CO2 show absorption signals in two distinct infrared bands at room temperature in Supplementary Fig. 9c,d, that is, 2,380–2,300 cm$^{-1}$, which is associated with CO2 molecules on the sample surface, and 1,500–1,430 cm$^{-1}$, which is typically observed for CO$_3^{2-}$ (ref. 26). 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 infrared absorption is observed for LSTMNA and LSTCNA. To test the ability to adsorb CO2 at elevated temperature, LSTMNA was subjected to in situ infrared tests between 400 and 1,200 $^\circ$C. As Fig. 3a,b reveal, both infrared bands remain visible up to 1,200 $^\circ$C, suggesting that both CO2 and carbonate species remain adsorbed, due to strong bonding with this titanate’s surface. Temperature Programmed Desorption sheds further light on the adsorption/desorption behaviour. Figure 3c shows how physisorbed CO2 is desorbed below 100 $^\circ$C, whereas chemisorbed CO2 is retained until much higher temperatures. For Cr/Mn-substituted titanate, the strongest desorption is extended to approximately 800 $^\circ$C, with concomitant increased adsorption capacity by an order of magnitude as compared to LST$_{O^+}$ (0.043 versus 0.0056 ml m$^{-2}$, respectively). These results are further corroborated by TGA in pure Ar atmosphere on reduced titanate samples that have subsequently been treated in CO2 at room temperature for 60 min, shown in Supplementary Fig. 9e. Much enhanced weight loss and continued desorption between 800 and 1,200 $^\circ$C is observed for all Cr/Mn-substituted samples as compared to LST$_{O^+}$, which desorbs almost all CO2 below 800 $^\circ$C. This is obviously also much improved when compared to amine-grafted oxides, which typically desorb below 500 $^\circ$C (refs 20, 21).

Theoretical calculations were carried out to construct a tentative mechanism for CO2 adsorption and activation on the titanate surface in conjunction with exsolved Ni nanoparticles and oxide vacancy defects. Before considering the presence and effect of such oxide vacancies however, we first study the CO2 chemisorption behaviour on the boundary of a Ni cluster and SrTiO$_3$ pristine surface (110), see Supplementary Fig. 10. As shown in Fig. 4a and Supplementary Fig. 11c, upon adsorption, low energy scenarios are found for CO2 forming a bidentate configuration including a carbonate formation (Supplementary Fig. 11a). Lowest adsorption energies of $-$2.23 and $-$2.60 eV are calculated for the configurations in which the carbon atom of CO2 binds with a Ni atom from the cluster, whereas one of CO2’s oxygen atoms (O1) attaches to an hcp site on the titanate surface, interacting with two Sr atoms and one Ti atom. With a calculated bond length of 1.906 Å for C–Ni, a strong interaction is expected. The Sr–O1 and Ti–O1 distances are 2.490 Å and 2.194 Å, respectively, which differ substantially from bulk strontium titanate (2.767 Å for Sr–O (ref. 27) and 1.952 Å for Ti–O from experimental observations)$^{28}$. The C–O1 bond length is elongated to 1.403 Å and the O–C–O angle is bent to 120.9$^\circ$ relative to the gaseous values of 1.18 Å and 180.0$^\circ$, respectively. This suggests that apart from a strong interaction between adsorbed CO2 and the Ni/SrTiO$_3$ surface, the distorted CO2 seems highly activated. Furthermore, by binding another CO2 molecule to the previously adsorbed oxygen atoms of CO2, such as O2 atom in Fig. 4a, these bidentate configurations could
be basic configurations to further generate carbonate, which may play a role as shown in our infrared experimental results. Contour plots shown in Fig. 4a indicate that the Ni cluster donates electron charge to the adsorbed CO$_2$ molecule; the charge density changes take place predominantly within the 2p orbitals of C, O, Ni and relevant surface atoms. The electrostatic interactions between

**Figure 3** | Chemical adsorption of CO$_2$ for a series of samples. (a,b) In situ infrared spectroscopy of CO$_2$ adsorbed on the reduced LSTMN$_{\text{A}^{-}}$ from 400 to 1,200 °C; (c) Temperature Programmed Desorption (TPD) test of CO$_2$ on the reduced samples from 50 to 1,000 °C in pure CO$_2$.

![Figure 3](image)

**Figure 4** | Theoretical calculations. Different adsorption configurations of CO$_2$ on (a) the (110) Ni/STO system surface and (b) defected site of the (110) Ni/STO system surface. The upper panels show side views while the middle panels give top-down views. Unit cells used in the calculations are marked by blue rectangles. Nickel is blue, strontium is green, titanium is pale, oxygen is red and carbon is grey. The bottom panels show contour plots of the electronic charge density difference for CO$_2$ adsorption on the (110) Ni/STO system surface (bottom left) and defected site of the (110) Ni/STO system surface (bottom right).
surface and CO₂, which would also affect the observed bidentate configuration, clearly suggest a strong chemical adsorption and activation, promoted by Ni exsolution.

Next we consider adsorption onto a titanate surface that includes oxygen vacancy defects. We use a simplified scenario of a single oxide vacancy site residing in close proximity to the Ni cluster on the SrTiO₃ (110) surface and simulate how CO₂ would approach and adsorb onto this site as shown in Supplementary Fig. 12. A distinctly different adsorption mechanism emerges now as compared to the vacancy-free titanate surface: in this scenario the CO₂ molecule exothermically dissociates into a CO moiety binding to the Ni cluster and an oxygen atom occupying the vacant surface site, with greatly enlarging of C–O₁ distance from gaseous value of 1.177 to 3.265 Å (Fig. 4b and Supplementary Fig. 12). The carbon atom of CO₂ is now binding to two Ni atoms, with bond lengths C–Ni₁ of 2.728–2.783 Å and 2.020–1.880 Å, respectively, whereas Cr/Mn-substituted and Ni-exsolving LSTM₀⁻ and LSTM₁⁻ cathodes perform best, with the lowest $R_p$ recorded of 0.67 Ω cm² at 800 °C and pH₂ = 1.0 bar. The symmetrical cell results are summarized in Supplementary Figs 14–16.

Electrolysis performance. Both symmetrical and full electrolyser cells were fabricated, comprising composite titanate cathodes with Ce₀.₈Sm₀.₂O₂₋ₓ. As can be seen in Supplementary Fig. 13, the cells contain dense electrolytes as well as porous electrodes of around 10 μm in thickness. AC impedance was performed on the symmetrical cells to assess the electrode polarization behaviour under reducing conditions, with pH₂ ranging from 0.20 to 1.0 bar. For all titanates, it was found that the series resistance $R_s$ was dominated by the YSZ electrolyte, confirming sufficient electronic conductivity as provided by the reduced titanates. And the ohmic resistance of electrode is negligible because the conductivity of electrodes is 3–4 orders of magnitude higher than that of the YSZ electrolyte. The electrode performance of all materials improved significantly with increasing pH₂ from 0.20 to 1.0 bar, with polarization resistances decreasing by 50–60%. LST₀⁺ was found to have the poorest performance (5.32–2.00 Ω cm²), whereas Cr/Mn-substituted and Ni-exsolving LSTM₀⁻ and LSTCN₀⁻ cathodes perform best, with the lowest $R_p$ recorded of 0.67 Ω cm² at 800 °C and pH₂ = 1.0 bar. The symmetrical cell results are summarized in Supplementary Figs 14–16.

The cells were used to perform direct CO₂ electrolysis under varying applied voltages, ranging from 1.2 to 2.0 V at 800 °C. The open circuit voltage of the cells was established by exposing the cathode and anode to 100% H₂ 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 CO₂ electrolysis mode can be found in Fig. 5. As expected from the previous findings, LSTM₀⁺ shows the poorest performance and CO₂ electrolysis with different cathodes at 800 °C; (b) short-term performances of CO₂ electrolysis at different voltages; (c) CO production and (d) current efficiency with different cathodes.

Figure 5 | Electrolysis performance. (a) I–V curves of CO₂ electrolysis with different cathodes at 800 °C; (b) short-term performances of CO₂ electrolysis at different voltages; (c) CO production and (d) current efficiency with different cathodes.
performance, reaching a maximum current density of 0.24 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. LSTMO$_{+}$ reaches a maximum current density of 0.53 A cm$^{-2}$ at 2.0 V. The nickel exsolving compositions show a further improvement, with maximum current densities of 0.91 and 0.79 A cm$^{-2}$ at 2.0 V for LSTMA$_{-}$ and LSTCN$_{A-}$, respectively. As the potentiostatic measurement in Fig. 5b shows, performances tail off somewhat over time, but a stable current density of 0.87 A cm$^{-2}$ seems to be attained for LSTMN$_{A-}$ at 2.0 V, a factor 3–4 times higher than observed for LSTO$_{+}$. Further evidence of these titanates’ suitability to reduce CO$_2$ at the cathode comes from inspecting the rate of CO production as measured by gas chromatography and corresponding Faradaic efficiencies at different applied voltages, shown in Fig. 5c,d. LSTMN$_{A-}$ and LSTCN$_{A-}$ yield 6.08 and 5.16 ml min$^{-1}$ cm$^{-2}$ of CO at 2.0 V and 800°C, respectively, corresponding to Faradaic efficiencies of 99.9 and 98.4%, respectively. When compared to unmodified LSTO$_{+}$, this constitutes a 400% improvement of performance. The effect of Ni exsolution yields a performance boost of 75–85% when comparing with Cr/Mn substitution only. Results have been summarized in Table 1.

One aspect that has been ignored so far is the effect of A-site deficiency on electrode performance. To enhance Ni exsolution, 5% A-site deficiency was introduced in the LSTMN$_{A-}$ and LSTCN$_{A-}$ materials, but the A-site deficiency itself may enhance electrode performance. The oxygen interstitial is present in LSTO$_{+}$, LSTMO$_{+}$, and LSTCO$_{+}$, though the oxygen vacancies are created and linked to redox active dopants such as Mn/Cr after reduction. However, the A-site deficiency would further produce higher oxygen vacancy concentration that may be positive to electrode activity enhancement. To study this effect, Cr/Mn-substituted LSTMA$_{-}$ and LSTCA$_{-}$ (5% A-site deficiency but no nickel substitution) were also used as cathode materials. Their performance, as indicated in Supplementary Fig. 17, is in between LSTO$_{+}$, LSTMO$_{+}$, and LSTCO$_{+}$, suggesting a positive electrocatalytic effect from the A-site deficiency. This may be the result of enhanced reducibility in such compositions and hence oxygen vacancy concentration, as proposed by Savaniu and Irvine$^{29}$. Still, the effect of Ni exsolution adds to the cathode’s electrochemical activity, as indicated by the superior performance.

To further understand the observed electrochemical performance in CO$_2$ electrolysis mode at 800°C for the different cathode materials, impedance spectroscopy was carried out under a range of applied biases, that is, 1.1–1.6 V. Similar trends are observed for all cathode materials, as shown in Supplementary Figs 18 and 19. First, series resistance, $R_s$, is stable and dominated by the electrolyte resistance, which is indicative of the titanates’

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**Table 1 | Performance with different cathodes.**

| Cathode | Applied bias (V) | LSTO$_{+}$ | LSTMO$_{+}$ | LSTCO$_{+}$ | LSTMA$_{-}$ | LSTCA$_{-}$ | LSTMN$_{A-}$ | LSTCN$_{A-}$ |
|---------|-----------------|-----------|-------------|-------------|------------|------------|-------------|-------------|
|         | 1.2             | 1.4       | 1.6         | 1.8         | 2.0        |
| Current density (A cm$^{-2}$) | 0.06 | 0.08 | 0.13 | 0.19 | 0.23 |
| CO production (ml min$^{-1}$ cm$^{-2}$) | 0.33 | 0.45 | 0.74 | 1.09 | 1.41 |
| Faradaic efficiency (%) | 78.7 | 80.4 | 81.4 | 82.0 | 87.7 |
| Current density (A cm$^{-2}$) | 0.08 | 0.20 | 0.32 | 0.45 | 0.51 |
| CO production (ml min$^{-1}$ cm$^{-2}$) | 0.50 | 1.26 | 2.05 | 2.95 | 3.36 |
| Faradaic efficiency (%) | 89.4 | 90.1 | 91.6 | 93.7 | 94.2 |
| Current density (A cm$^{-2}$) | 0.09 | 0.17 | 0.26 | 0.35 | 0.44 |
| CO production (ml min$^{-1}$ cm$^{-2}$) | 0.54 | 1.06 | 1.64 | 2.24 | 2.85 |
| Faradaic efficiency (%) | 85.8 | 89.2 | 90.2 | 91.5 | 92.6 |
| Current density (A cm$^{-2}$) | 0.10 | 0.22 | 0.36 | 0.51 | 0.66 |
| CO production (ml min$^{-1}$ cm$^{-2}$) | 0.63 | 1.39 | 2.34 | 3.41 | 4.43 |
| Faradaic efficiency (%) | 90.1 | 90.4 | 93.0 | 95.6 | 96.0 |
| Current density (A cm$^{-2}$) | 0.09 | 0.20 | 0.32 | 0.45 | 0.55 |
| CO production (ml min$^{-1}$ cm$^{-2}$) | 0.56 | 1.26 | 2.06 | 2.98 | 3.67 |
| Faradaic efficiency (%) | 89.0 | 90.1 | 92.1 | 94.7 | 95.4 |
| Current density (A cm$^{-2}$) | 0.16 | 0.36 | 0.54 | 0.69 | 0.87 |
| CO production (ml min$^{-1}$ cm$^{-2}$) | 1.06 | 2.42 | 3.67 | 4.76 | 6.08 |
| Faradaic efficiency (%) | 94.7 | 96.1 | 97.2 | 98.6 | 99.9 |
| Current density (A cm$^{-2}$) | 0.12 | 0.29 | 0.42 | 0.56 | 0.75 |
| CO production (ml min$^{-1}$ cm$^{-2}$) | 0.79 | 1.94 | 2.82 | 3.81 | 5.16 |
| Faradaic efficiency (%) | 94.1 | 95.6 | 96.0 | 97.3 | 98.4 |

LSTO$_{+}$(La$_{0.2}$Sr$_{0.8}$)$_{1.0}$O$_{3}$, LSTMO$_{+}$(La$_{0.2}$Sr$_{0.8}$)$_{0.95}$Ti$_{0.85}$Cr$_{0.1}$O$_{3}$, LSTCO$_{+}$(La$_{0.2}$Sr$_{0.8}$)$_{0.95}$Ti$_{0.85}$Mn$_{0.1}$O$_{3}$, LSTMA$_{-}$ (La$_{0.2}$Sr$_{0.8}$)$_{0.95}$Ti$_{0.85}$Mn$_{0.1}$Ni$_{0.05}$O$_{3}$, LSTCA$_{-}$ (La$_{0.2}$Sr$_{0.8}$)$_{0.95}$Ti$_{0.85}$Cr$_{0.1}$Ni$_{0.05}$O$_{3}$, LSTCN$_{A-}$ (La$_{0.2}$Sr$_{0.8}$)$_{0.95}$Ti$_{0.85}$Mn$_{0.1}$Ni$_{0.05}$O$_{3}$, LSTMN$_{A-}$ (La$_{0.2}$Sr$_{0.8}$)$_{0.95}$Ti$_{0.85}$Mn$_{0.1}$Ni$_{0.05}$O$_{3}$, LSTCN$_{A-}$ (La$_{0.2}$Sr$_{0.8}$)$_{0.95}$Ti$_{0.85}$Mn$_{0.1}$Ni$_{0.05}$O$_{3}$.

Comparison of CO$_2$ electrolysis with different cathodes under applied biases.
capability to provide an electronically conductive electrode backbone. In our full electrolyser, the ohmic resistance of electrode is negligible because the conductivity of titanates is 3–4 orders of magnitude higher than that of YSZ electrolyte. Second, polarization resistances, $R_p$, decrease with increasing voltages, which may be due to that the increasing potential leads to a stronger reducing potential that produces higher oxygen vacancy concentration in titanate and thus better ionic conductivity and CO$_2$ adsorption/activation, enhancing electrode kinetics. A change in the fermi level of the electron can also be expected to facilitate electrode polarizations by increasing applied potential. The electrode response seems to be dominated by two low frequency processes. One is related to gas conversion and its response diminishes upon increasing the applied voltage, as expected. The second process is tentatively attributed to dissociative adsorption of reactant species. This seems justified, as $R_p$ is largest for LST$_{O_+}$ (4.92–1.73 $\Omega$ cm$^2$ at 1.1–1.6 V) and decreases for LSTM$_{O_+}$ (2.86–0.82 $\Omega$ cm$^2$ at 1.1–1.6 V) to finally be lowest for LSTM$_{O_1}$ (1.41–0.51 $\Omega$ cm$^2$ at 1.1–1.6 V). Therefore $R_p$ seems to decrease with the electrode’s increasing ability to chemically adsorb and activate CO$_2$, with the best electrode performance observed for electrodes with both exsolved Ni and oxygen vacancies on its surface. The hetero-junction interface with Ni nanoparticles interacting with oxygen vacancy on titanate provides a synergy to facilitate electrode reaction. However, the catalytic activity of Mn itself in ABO$_3$ oxide is better than the Cr-doped sample, and the ionic conductivity of LSTM$_{O_1}$ is higher than that of LSTCO$_{O_+}$. The above two points would accordingly deliver better performance for LSTM$_{O_+}$ electrode even though LSTCO$_{O_+}$ has a higher oxygen vacancy concentration. The different cathode materials’ impedance responses at 1.6 V are summarized in Fig. 6.

The long-term stability of the exsolving cathode material LSTM$_{O_1}$ was assessed by performing CO$_2$ electrolysis for a period of 100 h at 1.3 V and 800 °C in 100% CO$_2$ atmosphere. As shown in Fig. 7a, a stable current density of 0.28 A cm$^{-2}$ is retained for the duration of the experiment. The stability of this material upon switching between oxidizing and reducing conditions was similarly assessed by redox cycling at 800 °C in alternating 5% H$_2$/Ar and air atmospheres, with subsequent CO$_2$ electrolysis at 1.3 V. As indicated by Fig. 7b and Supplementary Fig. 20, no performance degradation can be observed after 10 such redox cycles, demonstrating excellent stability of the active nanostructured surface of the titanate within the frames of these experiments. The anchoring of Ni nanoparticles to the perovskite lattice is expected to improve both long-term and redox stability, by preventing particle coalescence driven by surface energy reduction.

**Discussion**

In conclusion, we have shown exceptionally high performance for direct CO$_2$ electrolysis with near 100% Faradaic efficiency. The key is the tailored surface structure of doped strontium titanate that is in situ constructed through a combination of Ni particle exsolution and oxygen stoichiometry engineering. These active surface structures enable high-temperature chemical adsorption/activation of CO$_2$ and furthermore exhibit high-temperature stability for several tens of hours with significant
Characterization. Phase formations were confirmed by using X-ray diffraction (Cu Kα, Miniflex 600, Rigaku Corporation, Japan), and the data were refined by using the General Structure Analysis System software31. Scanning electron microscopy (SU-8010, JOEL Ltd, Japan) and high-resolution transmission electron microscopy (Tecnai F20, FEI Ltd, USA) were employed to investigate the exfoliation of nanotubes. XPS (ESCALAB 250Xi, Thermo, USA) with monochromatized Al Kα at hν = 1,486.6 eV was utilized to analyse elemental oxidation states. TGA was conducted on a Netzsch STA449F3 to calculate the oxygen stoichiometry. To this end, powder samples were first reduced in 5% H2/Ar at 800 °C for 20 h and TGA was subsequently performed on these samples from room temperature to 1,200 °C in air. The electrical properties of the reduced samples were examined using DC four-terminal method (Keithley 2000, Keithley Instruments Inc., USA) at an atmosphere of 5% H2/Ar between 650 and 800 °C. The H2O content in 5%H2/Ar or H2 streams were measured to be 0.5% and 1%, respectively corresponding to oxygen partial pressures of ~1 × 10⁻⁸ and ~1 × 10⁻¹¹ atm, respectively, at 800 °C. Approximately 2.0 g of the samples’ powders was pressed into pellets and sintered at 1,400 °C for 10 h in air to get dense samples. The conductivity tests, before the oxygen-ion conducting tests, the samples’ pellets were reduced at 800 °C for 20 h in 5% H2/Ar. All infrared spectra were collected using Fourier transform infrared spectrometer (VERTEX 70, Bruker). The powder samples were first reduced in 5% H2/Ar at 800 °C for 20 h and Temperature Programmed Desorption tests of CO2 were subsequently recorded from 50 to 1,200 °C in CO2 with a Micromeritics-Hiden Autochem II 2920/QC20.

Electrochemical characterization.Symmetric cells with 0.5-mm-thick YSZ and different titanate electrodes (1 cm²) were assembled and treated at 1,200 °C for 3 h in air. The current collector was made with silver paste (SS-8060, Xinluyi, 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 1,200 °C for 3 h in air. The current collector was made with silver paste (SS-8060, Xinluyi, China) and treated at 550 °C for 30 min in air. Electrochemical measurement was performed using an electrochemical station (IM6e, Zahner, Germany). The frequency range was 4 MHz to 100 Hz, and the voltage perturbation was 10 mV. The gas flow was controlled with mass flow meters (B58, Sontek). The electrochemical performance 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 cathode for 2 h in operation temperature. After that, the cathode would be sufficiently reduced and activated. Then the CO2 electrolysis was performed. The online gas chromatography (GC2010, Shimazu, Japan) was used to analyse the CO2 production and the CO2 production from the electrolysis cell electrodes under high-temperature coelectrolysis of steam and carbon dioxide. J. Power Sources 196, 7161–7168 (2011).

Methods Synthesis. Ceramic oxides including La0.9Sr0.1TiO3, (LST), La0.9Sr0.1Co0.7Fe0.3O3, (LSCF), (La0.9Sr0.1)0.95MnO3, (LSTM), (La0.9Sr0.1)0.95Cr0.1O3, (LSTC), (La0.9Sr0.1)0.95Ni0.05O3, (LSTN), (La0.9Sr0.1)0.95Fe0.1O3, (LSTF), (La0.9Sr0.1)0.95Mn0.1O3, (LSTMN), (La0.9Sr0.1)0.95Co0.1O3, (LSTCO), (La0.9Sr0.1)0.95Ni0.05O3, (LSTNO) and Ce0.9Sr0.1O2–δ powders were synthesized using a solid-state reaction method performed in air.19

Data availability. The data support that the findings of this study are available from the corresponding author(s) upon request.

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Author contributions

K.X. fully designed and supervised the project. J.T.S.I. supervised part of the project. L.Y. conducted the experimental work. M.Z. and C.L. carried out the theoretical calculations. All authors contributed to data analysis and gave approval to the final version of the manuscript.

Additional information

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