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In situ formation of oxygen vacancy in perovskite $\text{Sr}_{0.95}\text{Ti}_{0.8}\text{Nb}_{0.1}\text{M}_{0.1}\text{O}_3$ ($\text{M} = \text{Mn}, \text{Cr}$) toward efficient carbon dioxide electrolysis

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In this work, redox-active Mn or Cr is introduced to the B site of redox stable perovskite $\text{Sr}_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_{3.00}$ to create oxygen vacancies *in situ* after reduction for high-temperature CO_2 electrolysis. Combined analysis using X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and thermogravimetric analysis confirms the change of the chemical formula from oxidized $\text{Sr}_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_{3.00}$ to reduced $\text{Sr}_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_{2.90}$ for the bare sample. By contrast, a significant concentration of oxygen vacancy is additionally formed *in situ* for Mn- or Cr-doped samples by reducing the oxidized $\text{Sr}_{0.95}\text{Ti}_{0.8}\text{Nb}_{0.1}\text{M}_{0.1}\text{O}_{3.00}$ ($\text{M} = \text{Mn}, \text{Cr}$) to $\text{Sr}_{0.95}\text{Ti}_{0.8}\text{Nb}_{0.1}\text{M}_{0.1}\text{O}_{2.85}$. The ionic conductivities of the Mn- and Cr-doped titanate improve by approximately 2 times higher than bare titanate in an oxidizing atmosphere and 3–6 times higher in a reducing atmosphere at intermediate temperatures. A remarkable chemical accommodation of CO_2 molecules is achieved on the surface of the reduced and doped titanate, and the chemical desorption temperature reaches a common carbonate decomposition temperature. The electrical properties of the cathode materials are investigated and correlated with the electrochemical performance of the composite electrodes. Direct CO_2 electrolysis at composite cathodes is investigated in solid-oxide electrolyzers. The electrode polarizations and current efficiencies are observed to be significantly improved with the Mn- or Cr-doped titanate cathodes.

Currently, much attention is being focused on global warming and climate change, which is caused by the large consumption of fossil fuels, resulting in a large quantity of CO_2 emission^{1–5}. High-temperature CO_2 electrolysis in an oxide-ion conducting solid-oxide electrolyzer has the potential to directly convert electrical energy into chemical energy⁶. Using an external potential, CO_2 molecules are electrochemically reduced to CO at the cathode, whereas the oxygen ions are transported through the oxide-ion conducting electrolyte to the anode side to form oxygen gas^{7,8}.

A solid-oxide electrolyzer based on Ni-YSZ cermet has been widely used for high-temperature CO_2 electrolysis to generate CO fuel⁹. However, Ni metal can be easily oxidized to form NiO without a flow of reducing gas, which may cause a loss of electronic conductivity and failure of the electrode. In addition, poor resistance to redox cycling and the low stability performance limits its application in a solid-oxide electrolyzer. Moreover, the catalytic activity of Ni metal for the splitting of CO_2 is relatively high; carbon deposition most likely occurs and leads to the degradation of cell performance. Some reports have indicated that the deposition of carbon is likely caused by reactions that occur over the catalyst, and carbon deposition is likely to occur when hydrocarbons exist in the reactants^{10,11}. Recently, perovskite $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (LSCM) has been demonstrated to be an efficient ceramic cathode for direct CO_2 electrolysis in the absence of a reducing gas flowing over the composite cathode¹². However, this cathode is not ideally adapted to a strong reducing potential due to the p-type conduction mechanism of the LSCM, which results in a large electrode polarization resistance. In addition, our previous study demonstrated that strong reducing potentials can lead to adverse chemical and structural changes in LSCM under the electrolysis conditions¹³.

The perovskite strontium titanate is an active and redox stable material that possesses high n-type electronic conductivity upon reduction¹³. The metallic behavior of the electronic conductivity adapts well to the strong reducing atmosphere of the cathode under electrolysis conditions. Currently, more attention is being paid to the niobium doping of the B-site, where Nb^{5+} partially substitutes Ti^{4+} , which significantly improves the electrochemical properties^{14–16}. According to a previous report, the electrical conductivity of $\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_{3.00}$ that was pretreated at 1400°C for 5 h in a H_2/N_2 atmosphere reached approximately $340 \text{ S}\cdot\text{cm}^{-1}$ at 800°C in a reducing atmosphere¹⁷. Chen et al. also studied the effect of Ga doping in A-site-deficient $\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_{3.00}$ and determined that the sample with 10% Ga doping that were pretreated at 1400°C for 10 h in 10% H_2/Ar exhibited the highest electrical conductivity in a 10% H_2/Ar atmosphere at temperatures from 630 to 830°C ¹⁸. In addition,

other reports have also demonstrated the excellent redox stability of $\text{SrNb}_x\text{Ti}_{1-x}\text{O}_3$ materials after oxidizing and reducing treatments in air or humidified H_2 at high temperatures^{19,20}. Therefore, a composite cathode based on niobate-titanate would adapt to the reducing conditions of CO_2 electrolysis in an oxide-ion conducting solid-oxide electrolyzer. The niobate-titanate solid solution can be partially electrochemically reduced ($\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ and $\text{Nb}^{5+} \rightarrow \text{Nb}^{4+}$) at applied potentials, and the active Ti^{3+} or Nb^{4+} can act as a catalytic active site to further improve cathode performances with favorable kinetics in addition to significantly improving the electronic conductivity due to the high concentration of Ti^{3+} or Nb^{4+} in the B-sites.

In a solid-oxide electrolyzer, the insufficient adsorption of CO_2 is always the limitation at high temperature, which leads to the local starvation of CO_2 at the cathode, restricting the cathode performance

Figure 1 | XRD Rietveld refinement patterns of (a) oxidized STNO, (b) reduced STNO, (c) oxidized STNMO, (d) reduced STNMO, (e) oxidized STNCO and (f) reduced STNCO.

and current efficiency because linear CO₂ molecules in the absence of polarity do not easily chemically adsorb and activate, especially at high temperatures²¹. In general, the local starvation of CO₂ primarily leads to large electrode polarizations and low current efficiencies for CO₂ electrolysis at high temperatures²¹. In our previous report, efficient CO₂ electrolysis was demonstrated in an oxide-ion conducting solid-oxide electrolyzer with a cathode based on La_{0.2}Sr_{0.8}TiO_{3.1}, and promising electrode polarizations have been achieved under a series of external voltage loads²². However, mass transfer limitation, especially the insufficient adsorption of CO₂, was observed at the cathode, and the current efficiency for the production of CO was only approximately 36%²². It should be noted that the defect sites with oxygen vacancies on the surface of solid-oxide materials provide promising possibilities for the chemical adsorption of CO₂ because these defects may act as host sites to accommodate linear CO₂ molecules, which is expected to significantly increase the onset temperature of the chemical desorption of CO₂ and benefit the solid-oxide electrolyzer cathode with a certain amount of oxygen vacancies²³. In addition, the chemically adsorbed CO₂ molecules are expected to be strongly activated on these vacancy-related defect sites and be favorable for electrochemical reduction at high temperatures.

In this study, redox-active Mn or Cr is introduced into the B-site lattice of Sr_{0.95}Ti_{0.9}Nb_{0.1}O_{3.00} (STNO) to create oxygen vacancies *in situ* for high-temperature CO₂ electrolysis. The *in situ* formed oxygen vacancy is expected to not only chemically accommodate CO₂ molecules but also activate the electrode by enhancing the oxide-ion conductivity. The electrical properties, including the electronic conductivity, oxide-ion conductivity and n-type metallic behavior, have been investigated. The chemical desorption of CO₂ of the Mn-doped STNO is examined. Direct CO₂ electrolysis with a cathode based on Mn- or Cr-doped STNO is performed in an oxide-ion conducting solid-oxide electrolyzer.

Methods

All of the chemicals (99.9%) were purchased from SINOPHARM Chemical Reagent Co. Ltd. (Shanghai, China). Sr_{0.95}Ti_{0.9}Nb_{0.1}O_{3.00} (STNO) powders were synthesized using a traditional solid-state reaction method^{24,25}. Appropriate amounts of SrCO₃, TiO₂ and Nb₂O₅ powders were mixed together and ball-milled for 15 min in acetone. The dried powders were pressed into pellets and fired at 1300°C for 10 h in air^{26,27}. Sr_{0.95}Ti_{0.8}Nb_{0.1}Mn_{0.1}O₃ (STNMO) and Sr_{0.95}Ti_{0.8}Nb_{0.1}Cr_{0.1}O_{3.00} (STNCO) powders were similarly prepared using the method described above. (La_{0.8}Sr_{0.2})_{0.95}MnO_{3-δ} (LSMO) was also synthesized using the above method by mixing stoichiometric amounts of La₂O₃, SrCO₃ and MnO₂ with a heat-treatment temperature of 1100°C for 10 h in air²⁸. The Ce_{0.8}Sm_{0.2}O_{2-δ} (SDC) powders were prepared using a combustion method, in which the Sm₂O₃ and Ce(NO₃)₃·6H₂O powders were mixed and fired at 800°C for 3 h in air²⁹. The phase formations of the STNO, STNMO, STNCO, LSMO and SDC powders were analyzed by X-ray diffraction (XRD, 2θ = 3°·min⁻¹, D/MAX2500V, Rigaku Corporation, Japan). High-resolution transmission electron microscopy (HRTEM) analysis with selected area diffraction was performed to examine the oxidized and reduced STNO, STNMO and STNCO powders with a JEM-2100F field-emission transmission electron microscope (JEOL, Japan) operating at 200 kV. The specific surface area of the oxidized STNO and STNMO powders was tested using the brunauer- Emmett-teller (BET) method (low temperature adsorption of nitrogen, Quadrasorb, USA). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 to analyze the surface of the oxidized and reduced STNO, STNMO and STNCO powders. The binding energies were calibrated to the C_{1s} peak at 284.6 eV. TGA testing of the STNO, STNMO and STNCO samples was conducted using a thermal analyzer at 10°C·min⁻¹ in various atmospheres (STA449F3, NETZSCH).

Approximately 2.5 g of the STNO, STNMO and STNCO powders was pressed into bars and sintered at 1300°C for 10 h in air for the conductivity tests. Before the conductivity tests, the STNO, STNMO and STNCO bars were reduced at 1400°C for 10 h in 5% H₂/Ar. The DC four-terminal method was used for the conductivity test in a reducing atmosphere (5% H₂/Ar). The temperature ranged from 400 to 800°C at a rate of 3°C·min⁻¹. The conductivity was recorded with an online system with a time step of 10 s. The conductivity was recorded as a function of temperature from 400 to 800°C at the beginning and then as a function of the oxygen partial pressure (pO₂) from 10⁻²⁰ to 10⁻² atm. First, the flow rate of 5% H₂/Ar was controlled at 60 ml·min⁻¹ throughout the test to maintain the pO₂ at approximately 10⁻²⁰ atm. The air flow was controlled at a rate of 0.5 ml·min⁻¹ to change the pO₂ after terminating the input of 5% H₂/Ar. The total volume of the gas chamber was 12000 ml. The conductivity was recorded at 800°C. The conductivity and pO₂ were simultaneously measured using an online multi-meter (Keithley 2000, digital multimeter,

Keithley Instruments Inc., USA) and an online oxygen sensor (Type 1231, ZrO₂-based oxygen sensor, Noveltch, Australia), respectively. The testing time per 1 lgpO₂ was approximately 1 h below -13 and above -6, which is sufficient to maintain equilibrium; however, the oxygen partial pressure rapidly changed between -13 and -6 as the oxygen partial pressure was sensitive. The conductivity of the oxidized samples was tested from 400 to 800°C in air. In addition, the ion conductivity of the samples was tested as a function of temperature using the electron-blocking electrode method for the oxidized and reduced states, respectively^{30,31,35,36}. The ionic conductivity (σ_{ion}) can be calculated using the expression σ_{ion} = (1/R_{ion})/(L/A), where R_{ion} (in Ω) is the resistance obtained from the online multi-meter or the impedance data, L is the thickness of the sample (0.1–0.2 cm in the test) and A is the cross-sectional electrode contact area of the sample (2.0–3.0 cm² in the test). The ionic conductivity of YSZ pellets was tested and used as a reference.

The YSZ electrolyte support with a thickness of 1 mm was prepared by dry-pressing the YSZ powders into a green disk with a diameter of approximately 15 mm followed by sintering at 1550°C (2°C·min⁻¹) for 20 h in air. The two surfaces of the electrolyte were mechanically polished and ultrasonically washed in ethanol and distilled water. The slurries of the STNO/SDC, STNMO/SDC or STNCO/SDC cathodes were prepared by milling the STNO, STNMO or STNCO powders with SDC powders at a weight ratio of 65 : 35 in alpha-terpineol with the appropriate amounts of the cellulose additive. The LSMO and SDC powders were also mixed together at a weight ratio of 65 : 35 in alpha-terpineol with the appropriate amount of the cellulose additive to prepare the anode slurry. Then, the two types of slurries were coated onto the two sides of the electrolyte covering an approximately 1 cm² area, and the sample was sintered at 1000°C for 3 h in air. The current collector of the silver paste (SS-8060, Xinluyi, Shanghai, China) was printed on both surfaces of the electrodes. The silver wire (0.4 mm in diameter) was used to form the circuit using conductive adhesive (DAD87, Shanghai Research Institute for Synthetic Resins, Shanghai, China) and treated at 550°C for 0.5 h in air. The symmetric cell was prepared using the same method described above. The AC impedance spectroscopy for the different symmetric cells was studied at the open circuit voltage (OCV) using various H₂ and CO pressures at 800°C using an electrochemical station (IM6, Zahner, Germany). The frequency range was 1 MHz to 100 mHz, and the current perturbation was 10 mA.

Figure 2 | TEM images of (a) oxidized STNO, (b) reduced STNO, (c) oxidized STNMO, (d) reduced STNMO, (e) oxidized STNCO and (f) reduced STNCO.

The flow rates of the gases at $20 \text{ ml} \cdot \text{min}^{-1}$ and various hydrogen and CO pressures were controlled by the mass flow meter (D08-3F, Sevenstar, Beijing, China). The electrolysis cells were sealed into a homemade testing jig using ceramic paste (JD-767, Jiudian, Dongguan, China) for the electrochemical test. CO₂ electrolysis in the solid-oxide electrolyzers based on the STNO/SDC, STNMO/SDC or STNCO/SDC cathode was performed under various applied voltages at 800°C in CO₂. The AC impedance spectra and current density as a function of voltage curve (I-V curve) of the electrolysis cell were recorded. The frequency range was 1 MHz to 100 mHz, and the voltage perturbation was 10 mV. An online gas chromatograph (GC9790II, Fuli, Zhejiang, China) was used to analyze the CO concentration of the output gas from the electrolyzers. The current efficiency was calculated by dividing the tested value by the theoretical value of CO production calculated using Faraday's law.

Results and Discussion

Figs. 1 (a) and (b) present the XRD Rietveld refinement patterns of the oxidized and reduced STNO powders, respectively. The refinement of the oxidized and reduced samples yields χ^2 , wRp and Rp values of 1.46, 6.27% and 4.95% and 1.47, 6.52% and 5%, respectively, indicating close agreements with the experimental data. Based on the experimental and calculated results, the phase structure of both the oxidized and reduced samples is consistent with the perovskite structure with a space group of $\text{Pm}\bar{3}\text{m}^{32}$. The crystal cell parameter of the oxidized STNO is $3.9146(8) \text{ \AA}$, which is slightly smaller than that of the reduced STNO (i.e., $3.9191(8) \text{ \AA}$). The chemical oxidation states of Ti and Nb are +4 and +5 with ionic radii of 0.605 and 0.69 $\text{\AA}$, respectively, in the oxidized STNO. By contrast, a portion of the Ti and Nb has been transformed into Ti^{3+} (0.67 $\text{\AA}$) and Nb^{4+} (0.74 $\text{\AA}$) in the reduced STNO sample, which may cause the cell parameter expansion, even though oxygen loss is observed after the high-temperature reduction. Nevertheless, no phase transition is observed in the STNO even after the high-temperature treatment in a reducing atmosphere, which confirms the superior redox stability of the niobate-titanate ceramics. As demonstrated in Figs. 1 (c) and (d), the

XRD Rietveld refinement patterns of single-phase STNMO show the successful partial replacement of Ti with Mn at the B-site. The refinement of the oxidized and reduced samples yields χ^2 , wRp and Rp values of 1.196, 5.64% and 4.47% and 1.365, 5.90% and 4.53%, respectively. The cell parameter is $3.9139(4) \text{ \AA}$ for the oxidized STNMO, which is smaller than that of the oxidized STNO sample due to the smaller ionic radii of Mn^{4+} (0.53 $\text{\AA}$) in contrast to Ti^{4+} and Nb^{5+} . However, the cell parameter of the reduced STNMO increases to $3.9187(6) \text{ \AA}$ due to the partial transformation of Mn^{4+} , Nb^{5+} and Ti^{4+} to Mn^{3+} (0.645 $\text{\AA}$), Nb^{4+} (0.74 $\text{\AA}$) and Ti^{3+} (0.67 $\text{\AA}$), respectively, leading to expansion of the cell parameters in the reduced samples. A similar change is also observed for Cr-doped STNO in Figs. 1 (e) and (f). The refinement results of the oxidized and reduced STNCO yield χ^2 , wRp and Rp values of 1.329, 6.22% and 4.09% and 1.024, 6.40% and 4.37%, respectively. For the oxidized STNCO, the cell parameter is $3.91304(4) \text{ \AA}$, which is slightly smaller than that of the oxidized STNO because a small amount of Cr^{6+} (0.44 $\text{\AA}$) is present in STNCO. However, the cell parameters of the reduced STNCO increase to $3.91461(27) \text{ \AA}$ because of the transformation of Cr^{6+} , Nb^{5+} and Ti^{4+} to Cr^{3+} (0.615 $\text{\AA}$), Nb^{4+} (0.74 $\text{\AA}$) and Ti^{3+} (0.67 $\text{\AA}$), respectively, leading to the expansion of the cell parameters of the reduced STNCO. Fig. S1 presents the XRD patterns of the $\text{Sr}_{0.95}\text{Ti}_{0.9-x}\text{Nb}_{0.1}\text{Cr}_x\text{O}_3$ ($x = 0.1, 0.2$ and 0.3) powders after calcining in air at 1300°C for 10 h; however, a single-phase material is only achieved with $x = 0.1$ ($\text{Sr}_{0.95}\text{Ti}_{0.8}\text{Nb}_{0.1}\text{Cr}_{0.1}\text{O}_3$, STNCO). High-resolution transmission electron microscopy (HRTEM) analysis of the oxidized and reduced STNO sample indicates a lattice spacing of 0.280 and 0.284 nm for (110), respectively, as shown in Figs. 2 (a) and (b). The corresponding lattice spacing of the oxidized sample increases from 0.276 nm (110) to 0.279 nm (110) for the reduced STNMO sample (Figs. 2 (c) and (d)), which further confirms the

Figure 3 | XPS results of (a) Ti in oxidized STNO, (b) Ti in reduced STNO, (c) Nb in oxidized STNO and (d) Nb in reduced STNO.

lattice expansion of the reduced sample. In addition, the corresponding lattice spacing of the oxidized STNCO increased from 0.276 nm (110) to 0.277 nm (110) for the reduced STNCO in Figs. 2 (e) and (f), further confirming the lattice expansion of the reduced sample.

To confirm the elemental valence change, XPS analysis was performed to examine the oxidized and reduced samples. As observed in Fig. 3, a strong signal corresponding to Ti^{4+} and Nb^{5+} is observed in the oxidized STNO sample. However, a portion of the Ti^{4+} and Nb^{5+} is chemically reduced to Ti^{3+} and Nb^{4+} , respectively, by treating the STNO samples in a reducing atmosphere, as confirmed by the Ti^{3+} and Nb^{4+} signal, which is expected to significantly contribute to the electronic conductivity. Similar chemical state changes of the Ti and Nb elements were also observed in the STNMO sample before and after reduction at high temperature, as illustrated in Figs. 4 (a), (b),

(c) and (d). Mn^{3+} ($2p_{1/2}$), Mn^{4+} ($2p_{3/2}$) and Mn^{3+} ($2p_{3/2}$) peaks are observed at 653.40, 640.50 and 641.70 eV, respectively (Fig. 4 (f)), demonstrating the redox activity of the Mn element in oxides and that a small amount of Ti^{3+} remains present even in the oxidized sample. In addition, the XPS data indicates that Mn^{4+} is also chemically reduced to Mn^{3+} by treating the STNO samples in a reducing atmosphere. A similar chemical state change of $\text{Ti}^{3+/4+}$ and $\text{Nb}^{4+/5+}$ was also observed in the STNCO samples before and after reduction at high temperature, as shown in Figs. 5 (a, b, c and d). In addition, Cr^{3+} (575.8 and 585.9 eV) and Cr^{6+} (577, 580.5 and 588.7 eV) peaks are observed in Fig. 5 (e), indicating the presence of two elemental valences of $\text{Cr}^{3+/6+}$ in the oxidized samples. According to the fitting results, the $\text{Cr}^{3+}/\text{Cr}^{6+}$ ratio is $\sim 45.96:54.04$ for oxidized STNCO, which indicates that Cr^{6+} is the main chemical state in the oxidized

Figure 4 | XPS results of (a) Ti in oxidized STNMO, (b) Ti in reduced STNMO, (c) Nb in oxidized STNMO, (d) Nb in reduced STNMO, (e) Mn in oxidized STNMO and (f) Mn in reduced STNMO.

Figure 5 | XPS results of (a) Ti in oxidized STNCO, (b) Ti in reduced STNCO, (c) Nb in oxidized STNCO, (d) Nb in reduced STNCO, (e) Cr in oxidized STNCO and (f) Cr in reduced STNCO.

sample. By contrast, Cr^{3+} is the main chemical state for reduced STNCO, and all the Cr^{6+} is reduced to Cr^{3+} (576.1, 576.9, 579.2 and 586.1 eV) in a strong reducing atmosphere, as observed in Fig. 5 (f). The XPS data reveals that Cr^{6+} is chemically reduced to Cr^{3+} by treating the STNCO samples in a reducing atmosphere, which is expected to create oxygen vacancies, and the oxygen vacancy concentration is strongly related to the amount of low-valence ions at the B-sites. Thermogravimetry is commonly employed to analyze oxygen nonstoichiometry. As observed in Fig. 6, the oxidized STNO sample exhibits a 0.87% weight loss when heated at $10^\circ\text{C}\cdot\text{min}^{-1}$ from 1000°C to room temperature in a reducing gas, indicating a chemical formula of $\text{Sr}_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_{2.90}$ for the reduced sample. By contrast, the reduced STNMO sample possesses a chemical formula of $\text{Sr}_{0.95}\text{Ti}_{0.8}\text{Nb}_{0.1}\text{Mn}_{0.1}\text{O}_{2.85}$, which suggests that the Mn^{4+} in the oxi-

dized sample has been completely reduced to Mn^{3+} accompanied by the generation of oxygen vacancies and a change in the coordination number of the Mn ion in the B-sites. In addition, the oxidized STNO and STNCO samples are tested from room temperature to 1000°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in 5% H_2 /Ar. Fig. S2 (a) presents the weight change percentage of the oxidized STNO as a function of temperature upon heating in the reducing atmosphere. The weight loss reaches $\sim 0.8\%$ for the STNO sample due to the loss of oxygen caused by $\text{Ti}^{4+}/\text{Nb}^{5+}$ being reduced to $\text{Ti}^{3+}/\text{Nb}^{4+}$ under the reducing conditions, indicating a chemical formula of $\text{Sr}_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_{2.90}$ for the reduced sample. In comparison, the weight loss for the STNCO reaches $\sim 1.3\%$, as observed in Fig. S2 (b) (i.e., a chemical formula of $\text{Sr}_{0.95}\text{Ti}_{0.8}\text{Nb}_{0.1}\text{Cr}_{0.1}\text{O}_{2.85}$), which is also consistent with the loss of oxygen in a reducing atmosphere. However, the major part of the

Figure 6 | TGA of the samples in reducing gas from 1000 °C to room temperature: (a) STNO and (b) STNMO.

weight loss is due to the Cr-doped STNO, which suggests that the Cr^{6+} in the oxidized sample has been completely reduced into Cr^{3+} accompanied by the generation of oxygen vacancies, further confirming the XPS results for reduced STNCO presented in Fig. 5 (f).

The dependence of conductivities on the temperature and oxygen partial pressure ($p\text{O}_2$) is studied to investigate the electrical properties of the STNO, STNMO and STNCO samples. As observed in Fig. 7 (a), the conductivity of the reduced STNO, STNMO and STNCO samples display typical metallic behaviors with negative temperature coefficients in 5% H_2 /Ar, which indicates a typical n-

type conducting mechanism in reducing atmospheres. The reduced STNCO, STNMO and STNO samples exhibit similar conductivity values in 5% H_2 /Ar of approximately 36.3 , 54.5 and $60.2 \text{ S}\cdot\text{cm}^{-1}$ at 800°C , respectively. The conductivity of the reduced STNO sample is higher than that of the reduced STNMO and STNCO, which is most likely due to Mn or Cr doping at the B-sites of STNO. Therefore, the electron is consumed by the hole generated by the combination of the oxygen vacancy and atmospheric oxygen. The conductivities of the reduced STNO, STNMO and STNCO samples are strongly dependent on the $p\text{O}_2$, as observed in Figs. 6 (b), (c) and (d). The

Figure 7 | The electrical conductivity of STNO, STNMO and STNCO (a) as a function of temperature in 5% H_2 /Ar from 400 to 800°C and as a function of oxygen partial pressure (from 10^{-20} to 10^{-2} atm) at 800°C for (b) STNO, (c) STNMO and (d) STNCO.

Figure 8 | Ion conductivity of STNO, STNMO and STNCO as a function of temperature from 400 to 800 °C: (a) oxidized samples in air and (b) reduced samples in 5% H_2/Ar .

n-type conductivity rapidly decreases as the $p\text{O}_2$ increases from 10^{-16} to 10^{-15} atm, which is due to the conversion of Ti^{3+} to Ti^{4+} in the gradually decreasing reducing atmosphere at 800 °C. However, the conductivity does not change over a wide range of $p\text{O}_2$, which is most likely due to the rapid change in the $p\text{O}_2$ in this range, and the sample is not in an equilibrium state, which causes an inconsistent change in the conductivity. In addition, a significant decrease in the conductivity is observed for $p\text{O}_2$ above 10^{-4} atm due to the sufficient oxidation of Ti^{3+} to Ti^{4+} in the samples, and the sample finally transforms into a p-type conductor with a low conductivity at 800 °C in air. As observed in

Fig. S3, the conductivities of oxidized STNO and STNMO gradually improve with temperature, which indicates a typical p-type semiconducting behavior. The conductivity only reaches approximately $\sim 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ for oxidized STNO and $\sim 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ for STNMO at 800 °C in air due to an increase in the charge carriers generated by the combination of the oxygen vacancy created by the Mn dopant and the atmospheric oxygen. The material is redox stable; however, the conductivity is not stable in a wide range of $p\text{O}_2$ because the oxidation of the material leads to the loss of electronic conductivity. This material adapts well to a reducing condition but loses conductivity in an oxidizing atmosphere.

Figure 9 | TGA of reduced samples in Ar atmosphere: (a) STNO and (c) STNMO. Desorption of CO_2 for reduced samples in CO_2 atmosphere: (b) STNO and (d) STNMO.

Figure 10 | Microstructure of the solid-oxide symmetric and electrolyzer cells: (a) STNO/SDC-YSZ-STNO/SDC, (b) STNMO/SDC-YSZ-STNMO/SDC, (c) STNO/SDC-YSZ-LSMO/SDC and (d) STNMO/SDC-YSZ-LSMO/SDC.

With the formation of oxygen vacancies in the samples, the ionic conductivities of the Mn- or Cr-doped titanate are expected to remarkably improve. Fig. 8 shows the temperature dependence of the ionic conductivity of the oxidized and reduced samples in air and 5% H_2/Ar from 400 to 800°C, respectively. The ionic conductivities of the oxidized and reduced STNO samples improve with temperature and reach approximately 1.8×10^{-4} and $7.3 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ in air and 5% H_2/Ar , respectively, at 800°C. The reduced sample with a high concentration of oxygen vacancies strongly improves the ionic conductivity, which is approximately 3 times higher. In addition, the impedance spectra for the ionic conductivities of oxidized and reduced STNO at 800°C were also measured, and the results are presented in Figs. S4 (a) and (b), respectively^{35,36}. The calculated results show similar values for the ionic conductivities of STNO (i.e., 2.0×10^{-4} for oxidized and $7.1 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for reduced STNO). In Figs. 8 (a) and (b), the ionic conductivities of the oxidized and reduced STNMO as well as the STNCO samples reach 3.8×10^{-4} and $4.4 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ and 3.9×10^{-4} and 2.4×10^{-3} in air and 5% H_2/Ar at 800°C, respectively. In Fig. S4, the impedance spectra for the ionic conductivities of oxidized and reduced STNMO and STNCO at 800°C are also presented. The results have the same order of magnitudes as those in Fig. 8 (a) and (b). The introduction of redox-active Mn or Cr significantly enhances the ionic conductivity of STNMO or STNCO in contrast to STNO due to the creation of charge carriers and oxygen vacancies in the sample. However, the oxidized STNMO or STNCO sample exhibits low ionic conductivities even though these values are higher than those of the oxidized STNO sample, which are most likely due to insufficient oxygen vacancies; the oxygen vacancies are the charge carriers for oxide ion transport in the sample. However, the oxygen vacancy most likely prefers to exist at the grain boundary and further promote the ionic transport in sintered samples. Upon reduction, the STNMO or STNCO sample with a high concentration of oxygen vacancies exhibits significantly improved oxide-ion conductivity, which is approximately 1 order of magnitude higher in a reducing atmosphere at intermediate temperatures. Therefore, the oxygen vacancy defect site is expected to be able to accommodate the CO_2 molecules and enable chemical adsorption^{23,33}.

The adsorption of CO_2 was investigated for the STNO and STNMO samples using TGA tests in Ar and 100% CO_2 from room temperature to 1000°C at a rate of $10^\circ\text{C min}^{-1}$. In Figs. 9 (a) and (c), the weights of the reduced STNO and STNMO samples are unchanged in an Ar atmosphere in the temperature range of 200 to 1000°C, which are employed as references. By contrast, the weight

loss of the reduced STNO sample after CO_2 adsorption above 400°C reaches approximately 0.15%. The chemical desorption is observed at approximately 600°C (Fig. S5 (a)), which implies the presence of chemical adsorption of CO_2 on the reduced STNO sample. However, the weight loss of the reduced STNMO sample after CO_2 adsorption is substantially increased to 1%, and the strong chemical desorption has been extended to approximately 800°C, as shown in Fig. S5 (b). In addition, the specific surface area of the STNO and STNMO powders are similar to each other ($2.5 \text{ m}^2 \cdot \text{g}^{-1}$). The desorption of CO_2 was calculated, and the results are presented in Figs. 9 (b) and (d) for STNO and STNMO, respectively. The desorption volume of CO_2 is significantly enhanced to approximately $1.0 \text{ ml} \cdot \text{m}^{-2}$ catalyst for the Mn-doped STNMO sample, and the onset of the desorption temperature is as high as 800°C, which is near the decomposition temperature of common carbonates. The significant enhancement in the CO_2 adsorption on the reduced STNMO sample is due to the accommodation of CO_2 molecules on the oxygen-vacancy-related defect sites in the form of strong bonding between CO_2 molecules and substrates^{23,34}. It should be noted that the acidity of Nb/Ti is stronger than that of Mn, which restricts the chemical adsorption of CO_2 , even though oxygen deficiency is also observed in the reduced STNO sample. The strong chemical adsorption and activation of CO_2 are expected to significantly enhance the electrode performance and the CO_2 splitting under electrolysis conditions.

Figs. 10 (a) and (b) show the microstructure of symmetric cells with STNO/SDC-YSZ-STNO/SDC and STNMO/SDC-YSZ-STNMO/SDC configurations. Figs. 10 (c) and (d) show the configuration of STNO/SDC-YSZ-LSMO/SDC and STNMO/SDC-YSZ-LSMO/SDC, respectively, for the solid-oxide electrolyzers. The YSZ electrolyte supports are uniform and dense, with the porous electrode layers strongly adhered to the electrolyte. Fig. S6 shows the microstructures of electrodes with configurations of Ag-STNO/SDC-YSZ and Ag-STNCO/SDC-YSZ after tests, respectively. The YSZ electrolyte supports are quite uniform and dense; the porous electrode layers are approximately 10 μm in thickness and adhere to the electrolyte very well. Fig. 11 shows the AC impedance of the symmetric cells based on STNO, STNMO and STNCO tested at 800°C at various hydrogen partial pressures ($p\text{H}_2$). The series resistance (R_s) and polarization resistance (R_p) are equivalent to the first intercept and the difference between the first and second intercepts, respectively. The ionic resistance of the YSZ electrolyte, which primarily contributes to the R_s , is typically stable for a wide range of hydrogen partial pressures. However, as observed in Figs. 11 (a) and (b), the R_p of the symmetric cell based on STNO decreased from approximately 33 to 3 $\Omega \cdot \text{cm}^2$

Figure 11 | AC impedance plots for the symmetric cells for (a, b) STNO, (c, d) STNMO and (e, f) STNCO at various H_2 partial pressures at 800°C .

when the hydrogen partial pressure increased from 20% to 100%, which suggests that a stronger reducing atmosphere is beneficial for improving the electrode polarization. The stronger reducing atmosphere is favorable for the n-type electrical conductivity of the reduced STNO, STNMO and STNCO samples, which leads to improved electrode performances. By contrast, R_p of the symmetric cell based on STNMO or STNCO significantly improves from approximately 16 to $1.5\ \Omega\cdot\text{cm}^2$ (pH_2 : 10% to 100%) and 4.07 to $1.16\ \Omega\cdot\text{cm}^2$ (pH_2 : 10% to 80%) as the hydrogen concentration increased, which is most likely due to enhanced charge transfer and species diffusion in this composite electrode. Similar behavior has also been observed for the STNO, STNMO and STNCO composite electrodes in the symmetric cells in a CO/CO_2 atmosphere, with a CO concentration ranging from 1% to 5%, as observed in

Fig. 12. In this case, a stronger reducing atmosphere with a higher CO content is also favorable for increasing the electrical conductivity of the reduced STNO, STNMO and STNCO samples, leading to improved electrode performances. R_p of the symmetric cell based on STNO decreases from approximately 70 to $10\ \Omega\cdot\text{cm}^2$ for a CO concentration range of 1% to 5%. The R_p value based on STNMO and STNCO improved from 50 to $4\ \Omega\cdot\text{cm}^2$ and 12.38 to $3.28\ \Omega\cdot\text{cm}^2$ under the same conditions, respectively. However, this redox-stable electrode still exhibits promising polarizations even in a less reducing atmosphere, which is necessary for direct electrolysis of CO_2 at higher temperatures.

The direct electrolysis of pure CO_2 was investigated using three types of solid-oxide electrolyzers with cathodes based on STNMO, STNCO and STNO under a series of applied voltages at 800°C .

Figure 12 | AC impedance plots for the symmetric cells for (a, b) STNO, (c, d) STNMO and (e, f) STNCO at various CO partial pressures at 800°C.

Figure 13 | (a) I-V curves for three types of electrolyzers at 800°C in CO₂; (b) the performances of CO₂ electrolysis for the electrolyzer at 800°C in CO₂.

Figure 14 | *In situ* AC impedance plots for electrolyzers based on (a, b) STNO, (c, d) STNMO and (e, f) STNCO at various voltages with the flow of CO₂ at 800°C.

Fig. 13 (a) presents the typical curves of the current density as a function of voltage (I-V curves) of the electrolyzers for the direct CO₂ electrolysis. For the STNO cathode at 800°C, the maximum current density reaches approximately 250 mA·cm⁻² at 2.0 V, and the current density based on the STNMO and STNCO cathode greatly improves to approximately 348 and 332 mA·cm⁻² under the same conditions, respectively. Above 1.1 V, the current densities of the STNMO or STNCO composite electrodes increase steeply compared with the STNO composite cathode, which indicates that Mn or Cr doping significantly enhanced the cell performance for CO₂ electrolysis based on the STNMO or STNCO cathode. The chemical adsorption of CO₂ in the STNMO or STNCO composite electrode substantially contributes to the improved cell performances. The enhanced ionic conductivity of STNMO or STNCO is

also expected to improve the charge transfer in the composite electrode/YSZ interfaces. To study the electrolysis performance of the solid-oxide electrolyzers with the STNO, STNMO and STNCO cathodes, the cells were operated with the cathodes fed pure CO₂ at 800°C, as shown in Fig. 13 (b). The current density with the STNMO cathode reaches approximately 91, 138 and 200 mA·cm⁻² and that based on the STNCO cathode reaches approximately 86, 137 and 192 mA·cm⁻² at 1.2, 1.4 and 1.6 V, respectively; these values are much higher than those of the cell with the STNO cathode under the same conditions.

Fig. 14 presents the *in situ* AC impedance spectra recorded for a series of applied voltages ranging from 1.0 to 2.0 V at 800°C for the STNO, STNMO and STNCO composite cathodes. In general, the R_s values are stable. However, the R_p values considerably decrease as the

Figure 15 | (a) The production of CO; (b) current efficiency for the electrolyzers with STNO, STNMO and STNCO in the flow of CO₂ at 800°C.

applied voltage increases from 1.0 to 2.0 V. The applied voltage electrochemically reduces the composite cathode and enhances the mixed conductivity, resulting in enhanced electrocatalytic activity of the composite electrode. Two semicircles are observed in the impedance spectra (i.e., the high-frequency arcs (R_1) and low-frequency arcs (R_2)). At a high frequency, R_1 of the solid-oxide electrolyzers with cathodes based on bare STNO decreases to approximately $0.40 \Omega \cdot \text{cm}^2$. By contrast, R_1 for the cell with the STNMO cathode decreases to approximately $0.20 \Omega \cdot \text{cm}^2$ and is further enhanced under high applied potentials. The R_1 value for the cell with the STNCO cathode also decreases to approximately $0.22 \Omega \cdot \text{cm}^2$ at 2.0 V. R_1 is representative of the charge transfer at high frequency, and the improved R_1 indicates that the increased oxide-ion conductivity of STNMO or STNCO significantly improves the charge transfer. At a low frequency, the mass transfer, R_2 , dominates the electrode process of the solid-oxide electrolyzers due to the dissociative adsorption, gas conversion and species transfer at the three-phase boundary. R_2 for the cell based on the STNO cathode substantially improves from 3.59 to $1.05 \Omega \cdot \text{cm}^2$ for applied voltages of 1.0 to 2.0 V, suggesting improved gas conversion kinetics at high voltages. By contrast, R_2 for the cell based on the STNMO cathode significantly decreases to $2.47 \Omega \cdot \text{cm}^2$ at low voltages and is further enhanced to $0.51 \Omega \cdot \text{cm}^2$ at high voltages (the R_2 for an electrolyzer based on a STNCO cathode is significantly reduced from $2.54 \Omega \cdot \text{cm}^2$ at 1.0 V to $0.46 \Omega \cdot \text{cm}^2$ at 2.0 V), which demonstrates the significantly improved mass transfer due to the chemical adsorption of CO₂ in the composite cathode. Fig. S7 (a) presents the *in situ* AC impedance spectra for the electrolyzers based on the STNMO cathode under various CO₂ flow rates at 1.4 V. The R_s value is stable at 1.4 V; therefore, it is set to $0 \Omega \cdot \text{cm}^2$ in the figure. The low-frequency process, R_2 , is strongly related to the flow rates of CO₂; R_2 decreases with increasing flow rates of CO₂. In addition, an equivalent circuit is used for the impedance spectra in Figs. S7 (b, c and d). The results indicate that R_2 decreases from 1.48 to $1.32 \Omega \cdot \text{cm}^2$ for flow rates of CO₂ ranging from 10 to 30 ml·min⁻¹, which confirms the relationship between the gaseous mass transfer and the flow rates of CO₂ (i.e., the polarization performance is improved by increasing the mass flow of CO₂ through the cathode).

Fig. 15 shows the rate of CO production and the current efficiency of the electrolyzers with cathodes based on STNO, STNMO and STNCO for CO₂ electrolysis at various applied voltages in pure CO₂. As observed in Fig. 15 (a), the maximum CO productions for the cell based on the STNMO and STNCO electrodes are approximately 1.11 and $1.07 \text{ ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$, respectively, which are much higher than $0.78 \text{ ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ at 1.6 V with the

STNO electrode. As observed in Fig. 15 (b), for the STNO cathode, the maximum current efficiencies are approximately 70% in a flow of CO₂ at 800°C. By contrast, the maximum current efficiencies with the STNMO or STNCO cathodes increase by approximately 82% under the same conditions. Therefore, the solid-oxide electrolyzers based on the STNMO or STNCO cathodes exhibit better performance than those based on the STNO cathode. To validate the short-term stability, direct CO₂ electrolysis was performed at a fixed voltage of 1.6 V at 800°C for 24 h with pure CO₂ flowing over the cathode. As observed in Figs. S8 (a) and S9 (a), only a slight decrease in the current density occurs within the first few hours. However, the current density is stable, which confirms the excellent short-term stability of the STNMO and STNCO cathodes for direct CO₂ electrolysis. In addition, SEM and EDS mapping (Figs. S8 (b) and S9 (b)) were employed to analyze the cathode surface after short-term operation for high-temperature CO₂ electrolysis. No microstructure cracks are observed, which further confirms the stability of the material. The XRD results for the STNMO and STNCO cathodes are presented in Fig. S10 and Fig. S11. No other phases except for STNMO, STNCO, SDC and YSZ are present before and after the CO₂ electrolysis test at 800°C. Therefore, STNMO and STNCO are chemically stable against SDC and YSZ at high temperature. In addition, the long-term performance of the electrolyzer based on the STNMO cathode was evaluated at 800°C under an applied voltage of 1.4 V for direct CO₂ electrolysis, and the results are presented in Fig. S12. The results indicate that the current density is stable (approximately $90 \text{ mA} \cdot \text{cm}^{-2}$), which confirms the excellent long-term stability of the STNMO cathode for direct CO₂ electrolysis.

Conclusions

In this work, Mn- and Cr-doped perovskite niobate-titanate were investigated as potential cathode materials for high-temperature CO₂ electrolysis. The XRD, XPS and TEM results reveal lattice expansion in the Mn- or Cr-doped samples. In addition, the TGA results indicate that the *in situ* generated oxygen vacancies due to the reduction of Mn or Cr are responsible for the remarkable chemical adsorption of CO₂ at high temperatures. With Mn or Cr doping, the ion conductivities exhibit a robust enhancement; however, the electronic conductivity is significantly decreased. In addition to the promising electrode polarization based on the Mn- or Cr-doped electrodes, the current efficiencies of approximately 80% are notably improved by Mn- or Cr-doped electrodes for direct CO₂ electrolysis. Furthermore, the electrodes based on the Mn- or Cr-doped cathodes exhibit good stability for direct CO₂ electrolysis, which indicates that

both cathode types can be used as excellent cathodes for oxide-ion conducting solid-oxide electrolyzers.

- Pearson, P. N. & Palmer, M. R. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature* **406**, 695–699 (2000).
- Vasireddy, S., Morreale, B., Cugini, A., Song, C. S. & Spivey, J. J. Clean liquid fuels from direct coal liquefaction: chemistry, catalysis, technological status and challenges. *Energy Environ. Sci.* **4**, 311–345 (2011).
- Yasuo, I. Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond. *Coord. Chem. Rev.* **257**, 171–186 (2013).
- Stempien, J. P., Sun, Q. & Chan, S. H. Performance of power generation extension system based on solid-oxide electrolyzer cells under various design conditions. *Energy* **55**, 647–657 (2013).
- Yin, H. Y. *et al.* Capture and electrochemical conversion of CO₂ to value-added carbon and oxygen by molten salt electrolysis. *Energy Environ. Sci.* **6**, 1538–1545 (2013).
- Zhang, H. C., Wang, J. Y., Su, S. H. & Chen, J. C. Electrochemical performance characteristics and optimum design strategies of a solid oxide electrolysis cell system for carbon dioxide reduction. *Int. J. Hydrogen Energy* **38**, 9609–9618 (2013).
- Sridhar, K. R. & Vaniman, B. T. Oxygen production on Mars using solid oxide electrolysis. *Solid State Ionics* **93**, 321–328 (1997).
- Ni, M. 2D thermal modeling of a solid oxide electrolyzer cell (SOEC) for syngas production by H₂O/CO₂ co-electrolysis. *Int. J. Hydrogen Energy* **37**, 6389–6399 (2012).
- Fu, Q. X., Mabilat, C., Zahid, M., Brisse, A. & Gautier, L. Syngas production via high-temperature steam/CO₂ co-electrolysis: an economic assessment. *Energy Environ. Sci.* **3**, 1382–1397 (2010).
- Katsutoshi, N., Kulathuier, S., Kenichi, A. & Johannes, A. L. Carbon Deposition during Carbon Dioxide Reforming of Methane-Comparison between Pt/Al₂O₃ and Pt/ZrO₂. *J. Catal.* **197**, 34–42 (2001).
- Ebbesen, S. D. & Mogensen, M. Electrolysis of carbon dioxide in solid oxide electrolysis cells. *J. Power Sources* **193**, 349–358 (2009).
- Xu, S. S., Li, S. S., Yao, W. T., Dong, D. H. & Xie, K. Direct electrolysis of CO₂ using an oxygen-ion conducting solid oxide electrolyzer based on La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} electrode. *J. Power Sources* **230**, 115–121 (2013).
- Ruiz-Morales, J. C. *et al.* Disruption of extended defects in solid oxide fuel cell anodes for methane oxidation. *Nature* **439**, 568–571 (2006).
- Irvine, J. T. S., Slater, P. R. & Wright, P. A. Synthesis and Electrical Characterisation of the Perovskite Niobate-Titanates, Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-δ}. *Ionics* **2**, 213–216 (1996).
- Bochentyn, B. *et al.* The comparison of SrTi_{0.98}Nb_{0.02}O_{3-δ}-CeO₂ and SrTi_{0.98}Nb_{0.02}O_{3-δ}-YSZ composites for use in SOFC anodes. *J. Electroceram.* **28**, 132–138 (2012).
- Sudireddy, B. R., Blennow, P. & Nielsen, K. A. Microstructural and electrical characterization of Nb-doped SrTiO₃-YSZ composites for solid oxide cell electrodes. *Solid State Ionics* **216**, 44–49 (2012).
- Kolodiazny, T. & Petric, A. The Applicability of Sr-deficient n-type SrTiO₃ for SOFC Anodes. *J. Electroceram.* **15**, 5–11 (2005).
- Xiao, G. L., Dong, X. H., Huang, K. & Chen, F. L. Synthesis and characterizations of A-site deficient perovskite Sr_{0.9}Ti_{0.8-x}Ga_xNb_{0.2}O₃. *Mater. Res. Bull.* **46**, 57–61 (2011).
- Blennow, P., Hansen, K. K., Wallenberg, L. R. & Mogensen, M. Electrochemical characterization and redox behavior of Nb-doped SrTiO₃. *Solid State Ionics* **180**, 63–70 (2009).
- Gross, M. D. *et al.* Redox Stability of SrNb_xTi_{1-x}O₃-YSZ for Use in SOFC Anodes. *J. Electrochem. Soc.* **156**, B540–B545 (2009).
- Yue, X. L. & Irvine, J. T. S. Impedance Studies on LSCM/GDC Composite Cathode for High Temperature CO₂ Electrolysis. *ECS Transactions* **41**, 87–95 (2012).
- Li, Y. X. *et al.* Composite fuel electrode La_{0.2}Sr_{0.8}TiO_{3-δ}-Ce_{0.8}Sm_{0.2}O_{2-δ} for electrolysis of CO₂ in an oxygen-ion conducting solid oxide electrolyser. *Phys. Chem. Chem. Phys.* **14**, 15547–15553 (2012).
- Michael, N. Healing of oxygen vacancies on reduced surfaces of gold-doped ceria. *J. Chem. Phys.* **130**, 144702-1–144702-9 (2009).
- Kipyung, A., Sukwon, J., Vohs, J. M. & Gorte, R. J. A support layer for solid oxide fuel cells. *Ceram. Int.* **33**, 1065–1070 (2007).
- Hashimoto, S., Kindermann, L., Poulsen, F. W. & Mogensen, M. J. A study on the structural and electrical properties of lanthanum-doped strontium titanate prepared in air. *Alloy. Compd.* **397**, 245–249 (2005).
- Xiao, G. L. *et al.* Enhanced reducibility and conductivity of Na/K-doped SrTi_{0.8}Nb_{0.2}O₃. *J. Mater. Chem. A* **1**, 10546–10552 (2013).
- Fish, J. S. *et al.* Synthesis by spark plasma sintering of a novel protonic/electronic conductor composite: BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-δ}/Sr_{0.9}5Ti_{0.9}Nb_{0.1}O_{3-δ} (BCZY27/STN95). *J. Mater. Sci.* **48**, 6177–6185 (2013).
- He, H. P. *et al.* Low-Temperature Fabrication of Oxide Composites for Solid-Oxide Fuel Cells. *J. Am. Ceram. Soc.* **87**, 331–336 (2004).
- Jung, G. & Huang, T. Sintering temperature, microstructure and resistivity of polycrystalline Sm_{0.2}Ce_{0.8}O_{1.9} as SOFC's electrolyte. *J. Mater. Sci.* **38**, 2461–2468 (2003).
- Endo, A., Ihara, M., Komiyama, H. & Yamada, K. Cathodic reaction mechanism for dense Sr-doped lanthanum manganite electrodes. *Solid State Ionics* **86–88**, 1191–1195 (1996).
- Li, X. *et al.* Synthesis and electrical properties of Co-doped Y_{0.08}Sr_{0.92}TiO_{3-δ} as a potential SOFC anode. *Solid State Ionics* **179**, 1588–1592 (2008).
- Karczewski, J., Riegel, B., Gazda, M., Jasinski, P. & Kusz, B. Electrical and structural properties of Nb-doped SrTiO₃ ceramics. *J. Electroceram.* **24**, 326–330 (2010).
- Huang, T. J., Lin, H. J. & Yu, T. C. A comparison of oxygen-vacancy effect on activity behaviors of carbon dioxide and steam reforming of methane over supported nickel catalysts. *Catal. Lett.* **105**, 239–247 (2005).
- Pan, Y. X., Liu, C. J., Mei, D. H. & Ge, Q. F. Effects of Hydration and Oxygen Vacancy on CO₂ Adsorption and Activation on β-Ga₂O₃(100). *Langmuir* **26**, 5551–5558 (2010).
- Chen, C. C., Nasrallah, M. M., Anderson, H. U. & Alim, M. A. Impedance Response of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ Based Electrochemical Cells. *J. Electrochem. Soc.* **142**, 491–496 (1995).
- Patakangas, J., Ma, Y., Jing, Y. & Lund, P. Review and analysis of characterization methods and ionic conductivities for low-temperature solid oxide fuel cells (LT-SOFC). *J. Power Sources* **263**, 315–331 (2014).

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Author contributions

J.Z. conducted the experiments. K.X. and J.Z. drafted the manuscript. K.X. supervised the experiments. J.Z., K.X., H.W., Q.Q., W.Q., L.Y., C.R. and Y.W. were involved in the data analysis and discussions.

Additional information

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