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B-site doped perovskite ferrate for efficient anode of a solid oxide fuel cell with in situ metal exsolution

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Electronic supporting information containing the fitting of EIS, impedance spectra of cthode and oxygen stoichiometry from TGA and XPS can be retrieved online.

Abstract

Compared to Ni(O) cermet, an oxide anode is much better for a solid oxide fuel cell at suppresses coking and carbon deposition with carbonaceous fuels. Furthermore, a small amount of metal nanoparticles can enhance the electrochemical performance of the oxide anode while maintaining compatibility with the carbonaceous fuel when anchored on the oxide surface. In this study, ferrate-based perovskites ($\text{La}_{0.95}\text{Fe}_{0.80}\text{Ni}_{0.05}\text{Ti}_{0.15}\text{O}_3$, LFNT) with Ni^0 particles exsolution are investigated *via* B-site doping to increase the stability at 800 °C in H_2 atmosphere and electrocatalytic capability for fuel oxidation. Surprisingly, the B-site doped LaFeO_3 ($\text{La}_{0.95}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_3$, LFM) showed a high oxide-ion conductivity of 10 mS cm^{-1} with limited electronic conduction and further doping of Ti^{4+} or Ni^{2+} could increase the electronic conductivity to 30 Scm^{-1} and 100 Scm^{-1} at 800 °C for the reduced $\text{La}_{0.95}\text{Fe}_{0.8}\text{Mg}_{0.05}\text{TiO}_3$ (LFMT) and LFNT, respectively. The cell with LFNT anode on a $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ electrolyte shows a polarisation resistance of $0.32 \text{ }\Omega\text{cm}^2$ at 800 °C and a high power density of 600 mWcm^{-2} can be obtained when ceria is added *via* infiltration as a co-catalyst.

Introduction

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Development in oxide anodes is crucial to the utilisation of widely-available carbonaceous fuel as they suppress the carbon depositions associated with conventional Ni metal¹. Perovskite-type oxides with the nominal formula ABO_3 (A=large cations such as rare-earth or alkaline-elements, B=smaller cations of transition elements) are popular anode materials due to the special framework of $\langle BO_6 \rangle$ and the structural stability under a reducing or oxidizing atmosphere^{2, 3}. For example, perovskite-type titanates, chromate or manganite have been studied for efficient oxide anodes to suppress the deposition of carbon in a carbonaceous fuel⁴⁻⁶. Apart from the advantage in compatibility with the carbonaceous fuel, an oxide anode would also benefit from the redox stability by decreasing the volumetric expansion in contrast to Ni^0 , which is known for an expansion of 69.9% upon oxidation⁷. The redox stability could decrease the possibility of fracture of the adjacent electrolyte and shed light on the resolution through the re-oxidation process⁸ for the removal of sulphide produced by the sulphur impurities in the fuel. Nonetheless, oxide anodes are accused of inferior electrocatalysis to the oxidation of fuel at intermediate temperatures (600-800 °C) to conventional Ni(O)-based cermet⁹. Therefore, a high-performance anode catalyses the oxidation of fuel efficiently is also important to reducing the cost on cell manufacturing, increasing the power density and enhancing the fuel utilisation efficiency.

Infiltration of a small amount of metal catalysts on the surface of an oxide anode could be a promising method to enhance the performance and to lower the deposition of carbon¹⁰⁻¹⁴. However, the recent advancement in oxide anode showed that the *in situ* exsolution of metal nanoparticles in reducing atmosphere from an oxide anode containing reducible cations could enhance the stability of the metal particles by suppressing the thermally-induced grain growth and coking.¹⁵⁻¹⁸ Perovskite-type titanates are extensively studied as the parent materials for the exsolution of reduced metal particles¹⁹, but they require high temperatures (above 900 °C), extremely reducing atmosphere (e.g. dry H_2) or extended

reduction times to drive the outgrowth of metal nanoparticles²⁰. As for ferrate-based perovskites, LaFeO₃ perovskite with exsolved Pd, Pt, and Rh has been created and successfully applied as the well-known catalysts to control automobile emission which function at 400 °C,^{18, 21} but, in an electrochemical device, the stability, electric conductivity and compatibility with electrolyte impose extra demand to the material for exsolution. For a fuel cell working in the temperature range between 600 and 800 °C, the decomposition oxygen partial pressure of ferrate (LaFeO₃ and Sr₂Fe₂O₅) is quite close to that of humidified H₂-3% H₂O (**Figure 1**), while FeO/Fe₂O₃ and NiO can be reduced for the production of Fe⁰ and Ni⁰. The stability of LaFeO₃ perovskite can be achieved through the doping of less reducible cation, such as Mg²⁺, Ti⁴⁺, while the exsolution of metal particles can be achieved through the substitution of Ni for Fe in the oxide.

Figure 1. Theoretical electromotive force (EMF) of the oxygen pump between 1 bar oxygen and the equilibrium oxygen pressure in different decomposition reactions: *line 1*: $2\text{NiO} = \text{Ni} + \text{O}_2$; *line 2*: $2\text{Fe}_2\text{O}_3 = 4\text{Fe} + 3\text{O}_2$; *line 3*: $2\text{FeO} = 2\text{Fe} + \text{O}_2$; *line 4*: $4\text{LaFeO}_3 = 2\text{La}_2\text{O}_3 + 4\text{Fe} + 3\text{O}_2$ ²²; *line 5*: $4\text{TiO}_2 = 2\text{Ti}_2\text{O}_3 + \text{O}_2$; the dashed line is the Nernst potential of 3% H₂O-H₂ against 1 bar O₂. The open marks are experimental decomposition data for LaFeO₃ (circles^{23, 24}) and La_{0.6}Sr_{0.4}FeO₃ (square²⁵) and Sr₂Fe₂O₅ (triangles²⁶).

In this study, we presented a novel doping strategy on the well-studied LaFeO₃ by

replacing the Fe^{3+} on B site with stable cations, such as $\text{Mg}^{2+}/\text{Ti}^{4+}$ to decrease the structural instability and enhance the electric conductivity under a fuel condition up to 800 °C. A-site deficiency was also employed on this material to enhance the Ni^0 exsolution and suppress the phase segregation under a reducing atmosphere when 5% Ni was incorporated on the Fe site¹⁵. In particular, the doping of 20 % Mg^{2+} alone on Fe^{3+} site (as in $\text{La}_{0.95}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_3$, LFM) induced a high oxide-ion conduction (above 0.01 Scm^{-1} at 800 °C) and suppressed unexpectedly the electronic conduction. In addition, the thus prepared anodes, LFM, $\text{La}_{0.95}\text{Fe}_{0.8}\text{Mg}_{0.05}\text{Ti}_{0.15}\text{O}_3$ (LFMT) and $\text{La}_{0.95}\text{Fe}_{0.8}\text{Ni}_{0.05}\text{Ti}_{0.15}\text{O}_3$ (LFNT), showed a decent compatibility with the popular $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSGM) electrolyte up to 1100 °C. Cells with LFNT anode showed a small polarisation resistance, R_p , of $0.32 \Omega\text{cm}^2$ at 800 °C under H_2 fuel at 800 °C. Ni^0 nanoparticles of 20-30 nm in size exsolved on the surface of the anode were deeply submerged into the interior of the oxide matrix. This work provides significant insights into design of a superficial metal-particle exsolution at intermediate temperature on a stable perovskite-type ferrate oxide anode.

Experimental

Sample preparation

$\text{La}_{0.95}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LFM), $\text{La}_{0.95}\text{Fe}_{0.8}\text{Mg}_{0.05}\text{Ti}_{0.15}\text{O}_3$ (LFMT) and $\text{La}_{0.95}\text{Fe}_{0.8}\text{Ni}_{0.05}\text{Ti}_{0.15}\text{O}_3$ (LFNT) were synthesised via a conventional solid-state method²⁷. Stoichiometric amounts of precursors (La_2O_3 , Fe_2O_3 , MgO , NiO and TiO_2 , Macklin, 99.9%) were weighed and mixed in an agate mortar for 30 minutes and then the admixture was pelletized at 140 MP for better contact between the particles. The pellets were fired at 1250 °C in ambient air for 5 hours to obtain a monophasic material. Raw powders of LFMT and LFNT were obtained by crushing the pellet, and the particle size was further refined by grinding in a zirconia jar of a planetary ball-milling machine at 360 revolutions per minute for 1 hour. A dense $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSGM) electrolyte was prepared via the pressing of a commercial powder and calcination at 1500 °C for 5 hours²⁸. $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSC) powder for the cathode was synthesised via the

combustion method^{28, 29} where the precursors of $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Macklin, 99%), SrCO_3 (Aladdin, 99.5%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Macklin, 99%) and citrate acid (1:1 to the cation in molar ratio) as complexing agent were dissolved in diluted HNO_3 to obtained a clear solution, which was then dried at 80 °C on a hotplate. After the evaporation of water, the gel was ignited at 350 °C and the ashes were collected and calcined at 900 °C to obtain powder particles of sizes in nanometres.

Characterization

Room-temperature X-ray diffraction (XRD) of the sample was measured on a monochromatic diffractometer ($K_{\alpha 1}=1.5406 \text{ \AA}$, Persee XD-3, China) in the 2θ range from 15° to 90° at a step size of 0.02°. For compatibility with LSGM, LFNT or LFMT was mixed with LSGM in a 1:1 weight ratio and pelletized under 140 MPa before sintering at 900, 1000 and 1100 °C for 5 hours and then XRD was measured. The pellet from solid-state synthesis was cut into bars of 5 mm x 3 mm x 10 mm (around 20 % porosity) where four Ag wires (0.25 mm in diameter, Alfa Aesar, 99.99%) were attached to and the direct-current (DC) conductivity was recorded against temperature using a high-accuracy multimeter (Keithley 2100, USA). The conductivity of the sample was measured in air upon heating but in Ar-5% H_2 upon cooling after 5 hours' isothermal reduction at 800 °C and the oxygen partial pressure, $P(\text{O}_2)$, around the sample was monitored by a $P(\text{O}_2)$ sensor made of a 3 mol.-%- Y_2O_3 stabilised zirconia tube and two Pt electrodes. Ionic conductivity of the LFM pellet (8 mm in diameter and 2.5 mm in thickness) was measured by sandwiching the pellet between two dense $\text{Y}_{0.16}\text{Zr}_{0.84}\text{O}_{1.84}$ (8YSZ) pellets (10mm in diameter and 1.8 mm in thickness) as electron-blocking electrode after 10 hours' reduction³⁰. Silver paste was plastered on to the surface of pellets to avoid interface contact resistance. Because the 8YSZ pellets were considered to be of pure ionic conductivity, the stable DC conductivity obtained after a bias was applied on the electrode was considered as ionic conductivity. The ionic conductivity of LFM can be calculated since the conductivity of 8YSZ is already known³¹. X-ray photoelectron

spectroscopy (XPS) of the reduced samples was obtained on a Thermo ESCALAB 250Xi spectrophotometer using 150 W Al K_{α} radiation. Scanning electron microscopy (SEM) was performed with a JSM 7500 (JEOL, Japan) field-emission microscope and the transmitting electron microscopy (TEM) was carried out on a JFM 2100 microscope (JEOL, Japan) at an accelerating voltage of 200 kV.

Cell fabrication and testing

The powdered perovskites were mixed with an equal amount of vehicle containing 95 wt.% terpineol (95%, mixed polymorphs) and 5 wt.% polyvinylpyrrolidone ($M_w = 1300000$) for the slurry. The slurry was homogenized using an agate and mortar before being applied on the both sides of a dense LSGM electrolyte and then the cell was calcined in the air at 1100 °C for two hours to give an electrode of 0.5 cm² in area. The symmetrical cell was employed to measure the R_p of the electrode in pure H₂ or Ar-5%H₂ *via* electrochemical impedance between 500 °C and 800 °C during the cooling times.

A whole cell containing an LSC cathode and LFNT anode on LSGM electrolyte was used to obtain the discharge curve and impedance spectra at 800 °C, 750 °C and 700 °C. The LSC cathode was calcined at 950 °C for two hours on LSGM electrolyte after the calcination of anode at 1100 °C. The cell was mounted onto an alumina tube using a ceramic bond and the humidified H₂ gas flow (20 mL min⁻¹) was introduced at 600 °C upon the heating to 800 °C. The cell performance was measured after the anode was reduced at 800 °C for more than 5 hours. The chronoamperometry and impedance spectroscopy were measured on a *Zennium Pro* electrochemical workstation using a sine wave of 10 mV in the frequency range from 1 MHz to 48 mHz and the data were analysed using the *Z-man* software accompanying the electrochemical workstation.

Results and discussions

XRD diffraction and stability under fuel condition

In order to increase the stability of iron-based perovskite in the reducing atmosphere of

the fuel, the substitution of a non-reducible cation for the Fe^{3+} cation could be a viable way to increase the stability³². A-site deficient LFM, LFMT and LFNT with Mg^{2+} or Ti^{4+} replacing Fe^{3+} were proposed to reduce the Fe content and XRDs were shown in **Figure 2 (a)**. Monophasic perovskite can be obtained in ambient air and the powdered LFM and LFMT is stable after the reduction (**Figure 2 (a)**), while LFNT showed a tiny peak for Ni^0 (**Figure 2(b)**) after the reduction process. The single-phase perovskite-type LFNT in air and exsolution of Ni^0 after the reduction can be validated well through the detailed Rietveld refinement of the XRDs (**Figure 2(c,d)**). For a stoichiometric perovskite, the exsolution of metal particles can possibly induce the collateral exsolution of AO (**reaction 1**) or the formation of layered perovskite (**reaction 2**):

With the A-site deficiency in the parent perovskite, the exsolution of B^0 can produce a stoichiometric perovskite:

The construction of A site deficiency LaFeO_3 could induce the formation of oxygen deficiency or the formation of Fe^{4+} :

Unlike the doping in stoichiometric LaFeO_3 where the commensurate doping of Mg^{2+} and Ti^{4+} on Fe^{3+} site is needed to keep the charge neutrality, the A site deficiency in $\text{La}_{0.95}\text{FeO}_3$ gives the additional room for the Ti^{4+} as electron donor in the perovskite to maintain the Fe^{3+} in air.

As the anode of solid oxide fuel cell is adjacent to the electrolyte and the bipolar plate, the dramatic phase change of the perovskite will cause additional expansion/contraction and thus destroy the integrity of other components³³. The unit cell of the oxides at room

temperature before and after the reduction process was calculated and presented in **Table 1**, where one can see that the volumetric expansion due to the reduction process is under 1 %. Barnett *et al*³⁴ studied the stability of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ in reducing atmosphere and found that $\text{SrTi}_{0.3}\text{Fe}_{0.7}\text{O}_3$ decomposed to produce extra Fe^0 and Sr_2TiO_4 phases after a reduction at 800 °C, but $\text{SrTi}_{0.4}\text{Fe}_{0.6}\text{O}_3$ is resistant against reduction. $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.7}\text{Ti}_{0.3}\text{O}_3$ ³⁵ and $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ ³⁶ was found to maintain a perovskite phase after the reduction at 800 °C. The stability difference between $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.7}\text{Ti}_{0.3}\text{O}_3$ and $\text{SrTi}_{0.3}\text{Fe}_{0.7}\text{O}_3$ indicates that the donor doping on A site could stabilise the perovskite structure against reduction.

Figure 2. (a) XRD patterns of the LFMT, LFM and LFNT before and after reduction in 5% H_2 at 800 °C. The black and red lines are for those in air and after reduction, respectively. The shifting of the main peaks is highlighted in the right side of (a) and the peaks for Ni^0 in the reduced LFNT is highlighted in (b). The XRD patterns for LFNT in air and after reduction is simulated in (c) and (d), where the vertical ticks are the theoretical peak positions for LFNT and Ni^0 . The symmetry of perovskite unit cell is $Pbnm$.

Table 1. Unit cells of LFM, LFMT and LFNT before and after reduction. Unit cell of LSGM is provided for comparison.

	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
LFM	5.5193(4)	5.5447(6)	7.8546(8)	240.33(5)
LFMT	5.5496(7)	5.5425(6)	7.8181(6)	240.47(5)
LFNT	5.5449(9)	5.5323(7)	7.837(1)	240.41(6)
LFMR	5.5277(7)	5.5672(7)	7.8753(9)	242.36(7)
LFMTR	5.5465(2)	5.5600(3)	7.8808(4)	243.04(1)
LFNTR	5.5408(5)	5.5581(3)	7.8277(7)	241.07(2)
LSGM	5.5340(3)	5.5183(2)	7.8420(4)	239.48(2)

Good chemical compatibility between the electrode material is important for the assembly of different component as well as for the long-term operation of a fuel cell³⁷. For example, the NiO oxide is reactive with LSGM electrolyte even at temperatures as low as 600 °C for the production of insulating $\text{SrLaGa}_3\text{O}_7$, SrLaGaO_4 , MgO etc.^{38, 39}. These insulating materials will block the transport of oxide ion and the reaction site on triple phase boundaries, inducing an increased R_p . In order to avoid these issues La_2O_3 -doped ceria (LDC) is normally used as the buffer layer to prevent the reaction between the electrode and LSGM electrolyte,⁴⁰ since pure CeO_2 showed a significant reaction with LSGM due to the loss of La^{3+} from the perovskite to ceria causing the formation of insulating phases⁴¹. As of LFNT or LFMT, the La content in the perovskite is quite similar to that of LSGM and thus it can possibly decrease the reactivity of these materials for the insulating phases. Because LFNT and LSGM share the perovskite structure, LFNT XRDs are quite similar to that of LSGM. XRDs (**Figure 3**) of LSGM, LFNT and their pelletized mixture treated at 900, 1000 and 1100 °C for 5 h show no extra peaks except for the perovskite phases in the mixed content. However, LSGM is at a higher angle as in the enlarged peak around 32.25°. After a calcination at 1100 °C, the main peak of LFNT did not vary at all, indicating minor or no reactivity. More importantly, no extra

peaks for insulating phases were found. The compatibility of LFMT and LSGM was also conducted and no secondary phases were found up to 1100 °C either.

Figure 3. XRD pattern of the mixed powders (LSGM+LFNT) at 1100 °C (1), 1000 °C (2) and 900 °C (3) in comparison with the single-phase LSGM (4) or LFNT (5).

Thermogravimetric analysis (TGA) and electric conductivity

The valence variation of cations and loss of oxygen under a fuel condition would cause dramatic change in the physical property of an oxide material. TGA under a 5% H₂ gas (**Figure 4(a)**) indicates that LFM, LFMT and LFNT lost a weight in the range from 0.61% to 0.84% during the temperature rise to 800 °C and the following isothermal period. A two-stage weight loss of LFM corresponding to the Fe^{4+/3+} and Fe^{3+/2+} transition was found: i.e., one at 300 °C and the other at 480 °C, while the weight loss of LFNT and LFMT occurs at a temperature above 600 °C.

The DC conductivity of LFM (**Figure 4(b,c)**) in air is 2.43 Scm⁻¹ at 800 °C which decreases to 7.1 mS cm⁻¹ after the reduction in 5% H₂. On the contrary, LFMT and LFNT behaved like an insulator in air but after a reduction for 5 h they showed much higher conductivity (30-100 S cm⁻¹) with activation energies, E_a, below 0.1 eV, indicating that the electric conduction mechanism could be the small-polaron hopping²⁷. According to the XRD of LFNT after

reduction, Ni metal presented. However, the semiconductor-like conductivity at temperatures below 330 °C, suggested that the exsolved metal was not the main contributor to the conductivity. As a *p*-type semiconductor, LSF-based perovskite suffers from the decrease in conductivity under reducing atmosphere due to the reduction of Fe^{4+} : e.g. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Mn}_{0.1}\text{O}_3$ ⁴², $\text{Sm}_{0.95}\text{Ce}_{0.05}\text{FeO}_3$ ⁴³ and $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-\delta}$ ⁴⁴ showed a conductivity of 1 Scm^{-1} , 0.3 Scm^{-1} and 0.03 Scm^{-1} , respectively at 800 °C under H_2 . For SrFeO_3 with dominant Fe^{4+} has also been selected as parent material for anode fabrication: $\text{Sr}(\text{Fe},\text{Mo})\text{O}_3$ has been studied as the oxide anode material of an SOFC⁴⁵ and the conductivity is around 10 Scm^{-1} in H_2 at 800 °C and this could be attributed to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$ transition, and the conductivity can be greatly enhanced if the electron doping was performed *via* the substitution of La^{3+} for Sr^{2+} to modify the average valency of Fe and Mo cation⁴⁶.

Figure 4. (a) Thermogravimetric analysis of LFM, LFMT and LFNT in 5% H_2 up to 800 °C; DC conductivity of the samples (b) in air upon heating and (c) in 5% H_2 upon cooling after 5 hours' reduction. (d) total and ionic conductivity of LFM in 5% H_2 during the cooling process.

The arrow in (a) shows the heating direction and the activation energies, E_a , of the conductivity are included in (b, c, d).

As the charge carriers in LFMT and LFNT are related to the small polarons giving conductivities above 30 S cm^{-1} , the oxide-ion conduction could be too insignificant to measure directly without a blocking electrode. In contrast, the reduced LFM pellet (brilliantly yellow in colour) showed significant oxide-ion conductivity (**Figure 4(d)**). Compared to the conductivity from 4-probe configuration, the conductivity from the pellet with electron-blocking electrode is around 3.8 mScm^{-1} (53% of the total conductivity) at 800°C showed a higher E_a than the total conductivity, 1.09 eV vs 0.85 eV . The suppression of electronic conduction in LFM at high temperatures could be also attributed to the Mg^{2+} doping that decreases the percolation of possible $\text{Fe}^{2+}\text{-O-Fe}^{3+}/\text{Fe}^{4+}\text{-O-Fe}^{3+}$ in reducing atmosphere. Compared to LFM, the partial replacing of Mg^{2+} with Ti^{4+} could induce the variation of oxygen vacancies in the perovskite lattice after the reduction: i.e. the oxide-ion conduction in LFMT or LFNT should be close to 3.8 mScm^{-1} according to the similar weight loss in TGA and **equation (6)**.

where Kröger-Vink notation is used and B denotes the cations on B site¹⁵. Nonetheless, the oxide-ion conductivity at 800°C in air should be sufficient for an oxide anode to expand the reaction sites of H_2 oxidation in the functional layer.

X-ray photoemission spectroscopy

The change of Fe^{4+} in air to Fe^{2+} in reducing atmosphere is very likely to induce phase transition as in SrFeO_3 and SrFeO_2 with Fe^{4+} in $\langle\text{FeO}_6\rangle$ octahedron site and Fe^{2+} in square $\langle\text{FeO}_4\rangle$ planar coordination, respectively⁴⁷. The MgO doping in $\text{La}_{0.95}\text{FeO}_3$ increases the Fe^{4+} content for the electronic conduction in air³⁷, but the substitution of Mg^{2+} for Fe^{3+} stabilises the structure as it decreases the reducible Fe cations in the lattice in a reducing atmosphere. XPS for the reduced LFM, LFMT and LFNT (**Figure 5**) was presented in terms of the core levels

of Fe2p, O 1s, Ti2p and Ni2p. The Fe2p 3/2 spectra showed a predominant binding energy split for Fe³⁺ at 711 eV for LFM and 712 eV for LFMT and LFNT, respectively⁴⁸. The detailed calculation of Fe²⁺ represented by the peak at lower binding energy indicates that it accounts for 8.7%, 32.8% and 27.4% of the total Fe^{3+/2+} species for LFM, LFMT and LFNT, respectively. The high Fe²⁺ content in LFMT and LFNT facilitates the charge carrier transport along Fe³⁺-O-Fe²⁺ bonds, which is consistent with the high conductivity of them as the spinel type Fe₃O₄ with 1/3 divalent Fe²⁺ cation showing nearly a metallic conductivity. The split in O1s at 258.5-259 can be attributed to the <MO> (M=cation) bonds while those at higher binding energy could be related to the oxygen vacancies (at 531 eV) or absorbed OH group (at 533 eV)³⁷ as evidenced by the oxygen loss during the reduction process and an obvious weight gain during the cooling in the TGA curves. LFMT and LFNT with Ti⁴⁺ on B site showed a higher binding energy for O1s and Fe2p in <MO> bond than LFM as a result of the higher valency of Ti⁴⁺ than Fe^{2+/3+}. The binding energy of the Ti2p3/2 split in LFNT (458.7 eV) is close to that of Ti⁴⁺ in TiO₂ (458.5 eV), while the peak in LFNT (457.7 eV) is 1.0 eV lower and this could be related to the evolution of significant amount of Ti³⁺ in LFNT⁴⁹. The evolution of Ti³⁺ (62% of Ti³⁺ + Ti⁴⁺) could explain the extraordinarily high conductivity of LFNT after the reduction in Ar-5% H₂ at 800 °C. More importantly, the Ni2p peak of the reduced LFNT showed a predominant Ni⁰ peak at 853.2 eV and a minor oxide peak at 856.9 eV. The oxygen stoichiometries for LFM, LFMT and LFNT after the reduction, calculated using the valencies of the cations, are 2.79, 2.84 and 2.82 per perovskite formula (pf, **Table S1**), respectively, slightly lower than those from TGA result assuming an oxygen stoichiometry of 3 pf for the as-prepared perovskite. The calculated difference (0.06 to 0.09 pf) between the two techniques can be explained by the oxygen deficiency in the as-prepared sample or the variation from the surface to the bulk as XPS and TGA detects the very surface and the bulk material, respectively.

Figure 5. X-ray photoemission spectroscopy of LFM, LFNT and LFMT (if applicable) in terms of Fe2p (a), O1s (b), Ti2p (c) and Ni2p (d).

In the impedance spectra of the typical cell, its low- and high-frequency intersection with the Z' axis is generally the area-specific resistance (ASR) and ohmic resistance (R_s), respectively²⁷. The R_p value can be determined from the difference between ASR and R_s . The R_p of LFMT anode in 5% H_2 determined by EIS of the symmetrical cell (**Figure 6**) is quite large, $5.0 \Omega\text{cm}^2$, while that of LFNT is $2.1 \Omega\text{cm}^2$, indicating that replacing Mg^{2+} with Ni^{2+} can improve the electrocatalysis of the anode for H_2 oxidation. The improvement can be related to the exsolution of metal particles on the fuel/electrode interface. Moreover, the impedance of the LFNT electrode depends the H_2 concentration: the R_p is only $0.32 \Omega\text{cm}^2$ in H_2 , equivalent

to 16% of R_p value in 5% H_2 . After the measurement in H_2 , the impedance could be restored if the gas was switched to 5% H_2 , indicating that LFNT is stable in a very reducing atmosphere⁵⁰. The substitution of H_2 for 5% H_2 will decrease the oxygen partial pressure, P_{O_2} , from 10^{-21} to $10^{-19.6}$ bar to induce more oxygen vacancies in the perovskite and also increase the fugacity of H_2 to ease the adsorption and oxidation process of the fuel. Layered perovskites $Pr_{0.8}Sr_{1.2}(Co,Fe)_{0.8}Nb_{0.2}O_{4+\delta}$ (K–PSCFN)⁵¹, $La_{1.2}Sr_{0.8}Mn_{0.4}Fe_{0.6}O_4$ (K–LSMF)³³, $SrLaFeO_4$,⁵² and $Sr_3FeMoO_{7-\delta}$ (K–SFM)⁵³ with exsolved metal nano-particles have been synthesised by reducing the parent perovskites $Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$, $La_{0.6}Sr_{0.4}Mn_{0.2}Fe_{0.8}O_3$, $La_{0.6}Sr_{0.4}Fe_{0.95}Pd_{0.05}O_{3-\delta}$ (LSFPd) and $Sr_2FeMo_{0.65}Ni_{0.35}O_{6-\delta}$, at high temperature. R_p of the single-phase LFNT, $0.32 \Omega cm^2$, in H_2 is similar to K–PSCFN ($0.5 \Omega cm^2$) or K–LSMF with GDC ($0.32 \Omega cm^2$) at 800 °C. It should be noted that LFNT still maintains the original perovskite phase after reduction at 800 °C and the metal particles should be much less than the others. Compared to $SrFe_{0.75}Mo_{0.25}O_3$, $Sr_2FeMo_{0.65}Ni_{0.35}O_3$ and $Sm_{0.95}Ce_{0.05}FeO_3$ which have an R_p of 0.27, 0.163 and $0.084 \Omega cm^2$ at 800 °C respectively^{43, 45, 53}, LFNT showed higher R_p that could be related to the microstructures: we used ball-milled powders with larger particle sizes.

Figure 6. Electrode impedance of LFMT and LFNT at 800 °C measured in Ar-5% H_2 ($Lg(P_{O_2}/bar)$)

=-19.6, a, c) and in H₂ ($\lg(P_{O_2}/\text{bar})$ = -21.0, b, d). (c) and (d) are the Bode plots corresponding to the Nyquist plots in (a) and (c). The thickness of LSGMC electrolyte is around 950 μm in thickness.

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Structure characterizations

LFNT-based anode showed a much smaller R_p than LFMT-based one, while XRD, XPS results implied that the surface exsolution of Ni⁰ could be the reason. Thereafter, morphology of the LFNT anode after the tests under H₂ was evaluated using SEM and TEM (**Figure 7**). According to the SEM images, the grain-size of the porous LFNT electrode was around 1-5 μm and the surface of LFNT grains was coated with dense nodules of 20-30 nm in diameter. The detailed image of the nodules under TEM showed that they are actually spherical or elliptical beads partially embedded in the LFNT matrix. The analysis of d -spacings indicates that the beads could be metallic nickel in contact with LFNT matrix. Irvine et al¹⁷ pointed out that the nanoparticles exsolved from the oxide matrix could boast 30% submerged part in the titanate-based perovskite, but we found that the submerged part can be as high as 50% in a ferrate-based perovskite. The morphology of metal particles on the oxide substrate could enhance the anchoring of the nanoparticles on the matrix that was reported to suppress the size growth and coking under carbonaceous fuel⁵⁴.

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Figure 7. (a, b) Scanning electron microscopy images and (c, d) transmitting electron microscopy of the LFNT anode after test in H_2 at 800 °C. The arrow in (b) indicates the Ni^0 particles and the dashed line in (d) delimits the boundary between the Ni^0 particles and the perovskite matrix and the scale bar in (d) represents 10 nm.

Three fuel cells using LFNT anode with or without additional catalyst infiltration are prepared and tested on an LSGM electrolyte of 350 μm in thickness. Cell with bare LFNT anode showed a peak power of 280 mW cm^{-2} at 800 °C (**Figure 8**), while cells with Pd and ceria infiltration showed a peak power of 450 and 600 mW cm^{-2} , respectively. The infiltration of ceria-Pd co-catalyst will enhance greatly the performance of an LSCM or LST anode with mostly electronic conduction than either alone^{55, 56} and the improvement in performance

with either Pd or ceria in our case could be related to the ionic conduction of ceria or the superior electrocatalysis of Pd towards H₂ oxidation, respectively. The maximum power density of the cell with an LFNT-CeO₂ anode at 800 °C is higher than that with an La_{0.3}Sr_{0.7}Ti_{0.3}Fe_{0.7}O₃-CeO₂ anode on a 60-μm-thick (Sc₂O₃)_{0.1}(CeO₂)_{0.01}(ZrO₂)_{0.89} electrolyte (508 mWcm⁻²).³⁵ In the I-V curve, one can see that a de-curvature if the voltage is lower than 0.6 V, and this could be related to the oxidation of electrode under higher oxygen partial pressure^{12, 14}. The oxidation process will affect the oxide-ion conduction and electrocatalysis of the exsolved Fe⁰ on the anode towards the fuel oxidation process since no de-curvature was found in the cells with additional Pd or ceria infiltration. The addition of ceria in the LFNT anode enhanced the cell performance even more effectively than the one with Pd and this can be rationalised since the oxide-ion conductivity of the LFNT (on the magnitude of 10⁻³ Scm⁻¹) is much lower than that of ceria^{57, 58} under a reducing atmosphere as a result of the oxygen deficiency (0.05 per fluorite formula at 800 °C in H₂) created during the reduction of Ce⁴⁺ to Ce³⁺.⁵⁹ In our case, the addition of ceria as an oxide-ion conductor is more efficient than Pd in increasing the performance since there is metallic particles from the surface of LFNT anode. However, the durability of the cell (**Figure 8(d)**) with Pd catalyst at a constant voltage of 0.7 V showed some degradation (<10%) in the 24 hour's ageing at 700 °C. Degradation of a fuel cell with an LSCT anode was also found and this could be related to the microstructure change of the catalyst or the interaction between the oxide backbone and the superficial catalyst¹³. As Pd could maintain the metallic state under slightly reducing atmosphere (oxygen partial pressure $P_{O_2} < 10^{-5}$ bar at 800 °C), an increased oxygen partial pressure could induce the re-oxidation of LFNT and decrease the oxide-ion vacancies.

Figure 8. I-V and I-P curves for the cell with LFNT anode (a) with additional Pd (b) or CeO₂ (c) co-catalyst. (d) Initial-stage durability of the cell with LFNT-Pd anode under a constant bias at 0.7 V.

The R_p of the cells was also analysed using EIS (Figure 9) at open circuit voltage (OCV). The impedance of the whole cell with LFNT|LSGM|LSC at 800 °C showed an area-specific resistance of 0.79 Ωcm^2 , including an R_s of 0.28 Ωcm^2 and an R_p of 0.51 Ωcm^2 . Since the R_p of LSC was measured to be 0.16 Ωcm^2 (Figure S1), the R_p from the LFNT anode is calculated to be 0.35 Ωcm^2 , which is very close to the value of 0.32 Ωcm^2 from the symmetrical cell with an LFNT anode. Similarly, the R_p s for the LFNT-Pd and LFNT-CeO₂ anode in the whole cell at 800 °C was calculated to be 0.22 and 0.13 Ωcm^2 , respectively. The infiltration of Pd is supposed to increase the amount of superficial metal on the electrode and increase the

electrocatalysis of the fuel oxidation^{60, 61}, but a dramatic decrease has been obtained after the infiltration of ceria. As evidenced by the detailed fitting and analysis of the impedance spectra (**see ESI**), the H₂ oxidation of the cell with ceria was controlled by the surface diffusion or dissociative adsorption of gaseous species in contrast with the one with bare LFNT anode that is controlled by charge transfer process. The cell with additional Pd was limited simultaneously by the charge transfer and surface reaction process. A La_{0.2}Sr_{0.25}Ca_{0.45}TiO₃ (LSCT_{A-}) based anode with ceria infiltration showed an R_p of 1.5 Ωcm^2 at 800 °C¹⁴, which is around 10 time higher than LFNT-ceria anode in our study, indicating exsolved Ni⁰ particle in LFNT is critical to the high performance.

Figure 9. Electrochemical impedance spectroscopy of the cells with LFNT (a), LFNT+CeO₂ (b) and LFNT+Pd (c) as anode. The solid lines and open makes are fitted data with a modular circuit containing two serial Voigt elements and measured data, respectively. The thickness of LSGM electrolyte is 350 μm .

Conclusions

B-site doping on lanthanum ferrate perovskite has been adopted to increase the conductivity and stability in the fuel condition of an SOFC at 800 °C. It was found that substituting 20% of the Fe³⁺ sites with Mg²⁺ enhanced the ionic conductivity (above 0.01 S

cm⁻¹) and suppressed the electronic conduction of the perovskite under reducing atmosphere. The co-doping of Mg²⁺/Ti⁴⁺ and Ni²⁺/Ti⁴⁺ increased the electric conductivity by promoting and stabilizing the Fe³⁺/Fe²⁺ ratio, though the production of Ti³⁺ under reducing atmosphere at 800 °C could also contribute to the high conductivity in the LFNT perovskite (c.a. 100 Scm⁻¹). The cell with LFNT anode showed small R_{ps} (0.32 to 0.35 Ωcm²) at 800 °C and this could be related to the surface exsolution of Ni particles of 20-30 nm in diameter. With a slight infiltration of CeO₂ into the LFNT anode, a power of 600 Wcm² at 800 °C could be obtained even with an LSGM electrolyte of 350 μm in thickness.

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With engineering on the A-site deficiency and $\text{Ti}^{4+/3+}$ stabilization, Ni^0 exsolves and embeds partially in perovskite under in-situ reduction.